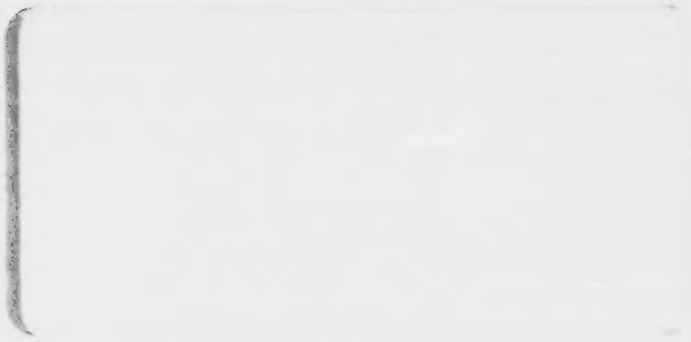

SHERIDAN TECHNICAL ASSOCIATES INC.

Consulting Research Laboratory Services

FINAL REPORT

FLUID CATALYTIC CRACKING OF NON-CONVENTIONAL GAS OILS BY AN OCTANE-ENHANCING CATALYST AND A METALS TOLERANT-CATALYST

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TABLE OF CONTENTS

	PAGE NO.
Executive Summary	1
Sommaire Executif	4
Recommendations	7
Introduction	8
Background	8
Experimental	
Feedstock Characterization	14
Catalyst Characterization	18
The Microactivity Test	20
Yield Calculations	22
Experimental Design	
Choice of Operating Variables	27
Range of Operating Conditions	29
Kinetic Modelling of FCCU Reactor	32
Results and Discussion	36
Results of Feedstock Studies	37
Results of Catalyst Studies	42
Cracking Characteristics of Gas Oils	52
IPL Gas Oil	57
Coleville Gas Oil	66
Lloydminster Gas Oil	77
Suncor Gas Oil	88
Shale Oil	98
CANMET Gas Oil	108
Comparison of Octane Enhancing and Metals Tolerant Catalyst	118
Coke Formation and Catalyst Deactivation	120
Conclusions	131
References	133
Appendix 1.	
Reactor Kinetic Model	
Appendix 2.	
Miscellaneous Information	

EXECUTIVE SUMMARY

This contract was undertaken to evaluate the cracking characteristics of a range of non-conventional gas oils over both metals tolerant (REY) and the newer octane enhancing (USY) catalyst. The work would establish the suitability of the various gas oils as FCCU feedstocks and their performance when cracked over the two different types of catalyst.

The gas oil samples included a "reference" gas oil from conventional Western Canadian crude (IPL) and gas oils from two heavy oils (Coleville and Lloydminster), a synthetic tar sands crude oil (Suncor), a shale oil and a CANMET primary upgraded product. The quality of the gas oils as FCC feedstock ranged from good to poor as shown by the variation in composition and physical properties: for example, the API gravity ranged from 16.2 to 25.0, the basic nitrogen content from 4570 ppm to 100 ppm, sulphur content from 2.86% to 0.24% and UOP k factor from 11.0 to 12.0.

The Mass Spec. analysis showed that the crackable components in the gas oils varied from 75.5 wt% for the IPL gas oil to 52.8% for the CANMET gas oil which essentially covers the range of good to poor FCC feedstock.

Samples of Davison DA-440 and Nova D equilibrium catalyst were chosen as typical metals tolerant (REY) and octane enhancing (USY) catalyst. The two catalysts showed similar microactivities (DA-440 70%, Nova D 72%) while the surface area and zeolite content was lower for the DA-440 catalyst (75.5 m2/g vs 101.9 m2/g, and 7.6% vs 10% respectively). The unit cell size for the Nova D catalyst (24.28 A°) was typical for USY zeolite while that for DA-440 (24.42 A°) was typical for REY zeolite. Both catalysts were based on a high alumina matrix for enhanced bottoms cracking.

For each catalyst/feedstock combination, nine microactivity tests were completed operating at three temperatures (470, 490 and 510C) and three C/O ratios (2, 4, and 6). To vary the C/O, the feed injection time was varied (90, 60 and 30 sec.) while the catalyst loading, WHSV, and feed injection rate were held constant at 4.2g, 20 hr-1, 1.4g/min. Over this range of reactor severities, the IPL gas showed gasoline overcracking, and most feedstocks achieved high conversion. Thus, it was concluded that the MAT unit operating range covered expected commercial unit severities.

The results from the experimental program were used to assess the influence of feedstock composition and catalyst type on conversion and product selectivity. A kinetic model which determines rate constants for cracking and catalyst decay, was further used interpreting the data. The influence of feedstock composition on achievable conversion was demonstrated for five of the six feedstocks by showing that the maximum measured conversion for each feedstock agreed closely with that predicted from the compositional data (100 - wt% refractory components). The compositional conversion constraint for the five feedstocks ranged from 52.8 to 80.6 wt% while the maximum measured conversion ranged from 54.5 to 79.1 wt%. The maximum difference between these two values was for the Suncor gas oil where the measured conversion was 4.7 wt% less than predicted. In contrast, the shale oil showed much poorer actual than predicted conversion (44.3 vs 81.1 wt%). This was attributed to excessive catalyst poisoning by nitrogen compounds. Both the shale oil and the CANMET gas oil showed high catalyst decay constants which limited both the achievable conversion and gasoline selectivity. In fact, the yield profiles for these two feedstocks were closely similar which is quite surprising considering completely dissimilar compositions.

The other three non-conventional gas oils (Coleville, Lloyd and Suncor) although of much better feedstock than the shale oil and the CANMET gas oil, showed lower cracking rates than the IPL gas oil, indicating that less paraffinic gas oils may need more active catalyst to achieve optimum conversion. This was suggested both from the kinetic analysis and the plots of conversion vs severity (C/O ratio) for the different feedstocks.

In comparing the activity of the two catalyst, it was found that the Nova D catalyst gave a higher maximum conversion for the paraffinic IPL gas oil (which agrees with the microactivities) while the DA-440 catalyst gave a high maximum conversion for all the non-conventional gas oils. This suggests that DA-440 is more active for non-paraffinic stocks and is more resistant to temporary catalyst poisons. The products selectivity plots - product yield vs converison - showed that the two catalyst were similar. For the better feedstocks, DA-440 was slightly more selective to gasoline while Nova D was more selective towards C3C4 production. In addition, at equal conversion, the Nova D (USY) catalyst produced a higher ratio of C3C4 olefin/paraffin than the DA-440 (REY) catalyst. These observations are in line with literature results which suggest that the USY dealuminated zeolites are less active than the REY zeolites and favour cracking to produce olefins rather than hydrogen transfer

which favours paraffin production and gasoline stabilization. The two catalysts showed little difference in coke selectivity for all the feedstocks. This contrasts with literature reports where a major feature of USY catalyst is good coke selectivity brought about by a decrease in the hydrogen transfer reaction. For three of the gas oils (Coleville, Suncor and Lloyd) it was noted that at equivalent severities, the Nova D catalyst produced less coke. However, higher severities were required for the Nova D catalyst to equal the conversion of the DA-440 catalyst thus mitigating any benefit from the decreased coking tendency. An analysis of the rate of coke formation based on Voorhies relationship indicated the the relative coking tendency of Nova D would improve w.r.t. DA-440 at the lower catalyst on-stream times of commercial operation.

For the range of non-conventional gas oils studies, it is concluded that further upgrading or improved FCC catalysts/reaction systems would be required for the shale oil and CANMET gas oil. The other three non-conventional gas oils would not normally warrant further upgrading, requiring only more active catalyst to optimize liquid product recovery.

Finally this combination of MAT results and feedstock and catalyst characterization provides an excellent basis for evaluation of a range of gas oils and catalysts. It is anticipated that the trends noted here would also be reflected in commercial operation, although more detailed modelling would be required to relate this data to a heat balanced riser cracker.

SOMMAIRE EXECUTIF

Ce contrat a été entrepris pour évaluer les caractéristiques de craquage d'une gamme de gazoles non classiques sur deux catalyseurs, un catalyseur tolérant les métaux (REY - Rare Earth Y - type zéolite) et un nouveau catalyseur qui améliore l'indice d'octane (USY - Ultra Stable Y - type zéolite). La recherche permettrait d'établir si les divers gazoles peuvent être utilisés comme stocks d'alimentation pour le craquage catalytique en lit fluidisé (CCF) et quelle est leur efficacité lorsqu'ils sont craqués sur deux types différents de catalyseur.

Les échantillons de gazole comprenaient un gazole de "référence" provenant d'un brut classique de l'Ouest canadien (IPL - Interprovincial Pipe Line) et des gazoles provenant de deux pétroles lourds (Coleville et Lloydminster), un brut de synthèse des sables asphaltiques (Suncor), un pétrole de schiste et un produit valorisé primaire du CANMET. La qualité des gazoles comme stocks d'alimentation pour le CCF variait de bonne à médiocre comme l'indiquent les variations de composition et de propriétés physiques : par exemple, la densité API variait de 16,2 à 25,0, la teneur en azote de base, de 4570 ppm à 100 ppm, la teneur en soufre, de 2,6 % à 0,24 %, et le facteur UOP, K, de 11,0 à 12,0.

L'analyse au spectomètre de masse a révélé que les proportions craquables du gazole variaient de 75,5 % en poids pour le gazole IPL à 52,8 % pour le gazole du CANMET, valeur qui délimite essentiellement la gamme de qualités, bonne à médiocre, des stocks d'alimentation pour le CCF.

Des échantillons de catalyseur à l'équilibre Davison DA-440 et Nova D ont été choisis comme catalyseur typique qui tolère les métaux (REY) et qui améliore l'indice d'octane (USY) respectivement. Les deux catalyseurs ont montré des micro-activités semblables (DA-440 70 %, Nova D 72 %), tandis que la surface des pores et la teneur en zéolite du catalyseur DA-440 étaient moindres, soit 75,5 m^2/g contre 101,9 m^2/g et 7,6 % contre 10 %, respectivement). La taille de la cellule cristalline pour le catalyseur Nova D (24,28 A) était typique pour le zéolite USY, tandis que celle pour le catalyseur DA-440 (24,42 A) était typique pour le zéolite REY. Les deux catalyseurs ont été placés sur une matrice d'alumine élevée pour favoriser le craquage des résidus.

Pour chaque combinaison catalyseur/stock d'alimentation, 9 essais de micro-activité ont été réalisés, à trois températures de réaction (470, 490 et 510 °C) et avec trois rapports catalyseur/pétrole (2, 4 et 6). Pour modifier le rapport catalyseur/pétrole, le temps d'injection du stock d'alimentation a été changé (90, 60 et 30 s), tandis que la masse de catalyseur, la vitesse spatiale horaire massique et le débit d'alimentation ont été maintenus constants à 4,2 g, 20 h^{-1} et 1,4 g/min respectivement. Dans cette plage de conditions du réacteur, le gazole IPL a montré craquage excessif, et la plupart des stocks d'alimentation ont présenté des taux de conversion élevés. Par conséquent, on a conclu que la plage de fonctionnement de l'appareil d'essai de micro-activité couvrait les conditions prévues pour la version commerciale.

Les résultats du programme expérimental ont été utilisés pour évaluer l'effet de la composition de l'alimentation et du type de catalyseur sur la conversion et la sélectivité de la production. Un modèle cinétique qui calcule des constantes de vitesse de craquage et des constantes de désactivation du catalyseur ont été en outre utilisées pour interpréter les données. L'effet de la composition de l'alimentation sur le taux de conversion réalisable a été démontré pour cinq des six stocks d'alimentation : en effet, le taux de conversion maximal mesuré pour chaque stock d'alimentation concordait étroitement avec les valeurs prévues à partir des données sur la composition (100 % en poids - constituants réfractaires). La limite de conversion due à la composition des cinq stocks d'alimentation variait de 52,8 à 80,6 % en poids, tandis que le taux de conversion maximum mesuré variait de 54,5 à 79,1 % en poids. L'écart entre ces deux valeurs a été le plus grand pour le gazole Suncor dont le taux de conversion mesuré a été de 4,7 % en poids inférieur au taux prévu. Par contre, le pétrole de schiste a présenté un taux de conversion réel de beaucoup inférieur au taux prévu (44,3 % contre 81,1 % en poids). Ce faible taux a été attribué à un empoisonnement excessif du catalyseur par des composés azotés de base. Le pétrole de schiste et le gazole du CANMET ont tous les deux présentés des constantes de désactivation du catalyseur élevées qui ont limité le taux de conversion réalisable et la production d'essence. En fait, les profils de rendement de ces deux stocks d'alimentation étaient très semblables, ce qui est assez étonnant compte tenu de leurs compositions tout à fait différentes.

Les trois autres gazoles non classiques (Coleville, Lloyd et Suncor), qui constituent en fait des stocks d'alimentation de beaucoup supérieurs au pétrole de schiste et au gazole du CANMET, ont présenté des taux de craquage inférieurs à celui du gazole IPL, ce qui indique que pour réaliser une conversion optimale des gazoles peu paraffiniques, il faudrait recourir à un catalyseur plus actif. Cette conclusion est ressortie de l'analyse cinétique et des courbes de conversion en fonction du rapport catalyseur/pétrole pour les différents stocks d'alimentation.

En comparant les activités des deux catalyseurs, on a constaté que le catalyseur Nova D avait un taux de conversion maximal plus élevé avec le gazole IPL paraffinique (ce que corroborent les micro-activités), tandis que le catalyseur DA-440 avait un taux de conversion maximal élevé avec tous les gazoles non classiques. Cela indique que le catalyseur DA-440 est plus actif avec des stocks non paraffiniques et résiste davantage aux poisons temporaires. Les courbes de sélectivité de la production (rendement-conversion) ont révélé que les deux catalyseurs étaient semblables. Avec les meilleurs stocks d'alimentation, le DA-440 a donné légèrement plus d'essence, tandis que le Nova D a donné plus de produits C3C4. En outre, à taux de conversion égal, le catalyseur Nova D (USY) a montré un rapport C3C4 oléfine/paraffine plus élevé que le catalyseur DA-440 (REY). Ces observations confirment les résultats publiés dans la documentation qui indiquent que les zéolites désaluminisés USY sont moins actifs que les zéolites REY et qu'ils favorisent au craquage la production d'oléfines plutôt que le transfert d'hydrogène qui favorise la production de paraffine et la stabilisation de l'essence.

Les deux catalyseurs ont donné des productions de coke très peu différentes avec tous les stocks d'alimentation. Ce résultat n'est pas en accord avec les rapports publiés dans lesquels on indique qu'une caractéristique importante du catalyseur USY est qu'il donne moins de production de coke lorsque la réaction de transfert d'hydrogène est réduite. Dans le cas de trois gazoles (Coleville, Sunco et Lloyd), on a noté que dans des conditions équivalentes, le catalyseur Nova D a produit moins de coke. Cependant, il a fallu pousser les conditions pour que le catalyseur Nova D présente un taux de conversion égal à celui du catalyseur DA-440, diminuant ainsi tout avantage que présente une faible tendance à la cokéfaction. Une analyse du taux de formation de coke, basée sur la relation de Voorhies, a révélé que la tendance relative à la cokéfaction du catalyseur Nova D approcherait la performance du catalyseur DA-440 dans des conditions d'exploitation commerciale, c'est-à-dire à de faible temps de séjour en circuit du catalyseur.

Dans le cadre des études sur les gazoles non classiques, on conclut qu'il faudrait continuer d'améliorer les systèmes catalyseurs/réaction de CCF dans le cas du pétrole de schiste et du gazole du CANMET, tandis que les trois autres gazoles ne justifiaient normalement pas une amélioration, si ce n'est l'utilisation d'un catalyseur plus actif.

On peut dire en conclusion que les résultats des essais de micro-activité, ajoutés à la caractérisation de l'alimentation et du catalyseur, constituent un excellent outil pour évaluer une gamme de gazoles et de catalyseurs. On s'attend que les tendances observées s'appliquent aussi aux systèmes commerciaux, même s'il faudrait pousser la modélisation pour établir une relation entre ces données et un réacteur de craquage (Riser) en équilibre thermique.

RECOMMENDATIONS

(1) Set up standard capillary gas chromatographic method to analyze reactor effluent and calculate gasoline and light cycle oil properties. Gasoline octane and LCO cetane are important economic factors in FCC operations.

(2) Use kinetic model to translate MAT data into heat balanced riser yields.

(3) Indentify catalyst poisons and evaluate procedures for mitigating the effect of excessive rates of catalyst decay either through feed pretreatment or catalyst/process modifications.

(4) Evaluate procedures for increasing conversion of naphthenoaromatics either through feed pretreatment or catalyst/process modifications.

INTRODUCTION

The work was carried out to fulfill a contract awarded in September 1986 to study the catalytic cracking characteristics of four non-conventional gas oils and a conventional gas oil using both metals-tolerant and octane enhancing catalysts.

CANMET provided the following non-conventional gas oils.

(1) SF-164. This sample was distilled from a Suncor hydrotreated synthetic crude.
(2) LHOF 12-1. This sample was distilled from a heavy crude pipeline blend obtained from the Coleville area of Saskatchewan.
(3) LHOF 16-2. This sample was distilled from a Lloydminster heavy oil. The oil was produced using a wet combustion EOR technique.
(4) Shale Oil. This sample was provided to CANMET by the New Brunswick Research and Productivity Council and was produced from the pyrolysis of New Brunswick shale. Again the gas oil fraction was obtained by distillation.

STA obtained a sample of conventional vacuum gas oil from a Canadian Refinery which was processing I.P.L. crude oil. The two catalysts used for the study were:

(1) DA-440 as the metals tolerant catalyst. A sample of equilibrium catalyst was obtained from a Canadian refinery.
(2) Nova D as the octane enhancing catalyst. A sample of equilibrium catalyst was obtained from Davison Chemical of Baltimore.

In June 1987, the contract was modified by including MAT runs for CANMET gas oil derived from Cold Lake VTB using the CANMET hydrocracking process. CANMET provided this sample.

BACKGROUND

It is recognised that Canadian Refiners will in the future have to rely increasingly on non-conventional oils to produce transportation fuels, as conventional Western Canadian oil reserves decline. To be acceptable to the Refiner, the gas oil portion of the non-conventional oil has to be amenable to processing by the major upgrading unit in a refinery, the fluidized catalytic cracking unit. The FCC complex essentially converts gas oils (boiling range 340C to 540C) into gasoline and distillate range material. Non-conventional gas oils can present a variety of problems to

the refiner because of their refractory nature and high level of heteroatoms and at times they need hydrotreating before being charged to the FCCU. However, it is economically advantageous when the straight run gas oil can be directly charged to the FCCU. Recent developments in the FCC process and catalyst now allow the cracking of the more refractory feedstocks.

Heavy oils and tar sands bitumens are thought to be the remains of oil deposits that have been biodegraded. This action selectively removes the paraffinic hydrocarbons and then the other saturate hydrocarbons from the oil. Thus, the remaining oils are very aromatic and somewhat refractory in the cracking process, tending to produce more light cycle oil (LCO 216-343C) and decant oil (343C+ material) and less gasoline and C3C4 hydrocarbons than conventional gas oils. In addition, because of the high sulphur content, they will produce significantly more H2S. They also tend to yield more light gas and coke than conventional gas oils because of their aromatic character. The liquid products produced from cracking these heavy oils are themselves very aromatic. This is a problem for the diesel cuts because of the poor diesel ignition quality of aromatic materials. On the positive side, the aromatic character produces high octane gasoline components and the oils are significantly lower in cost than conventional oils.

The value of the gas oil as FCC feedstock depends primarily on two characteristics:

(1) the percentage of components that can be converted to light products and
(2) the presence of problematic components which may reduce both catalysts' activity and selectivity for conversion.

The first characteristic can be estimated from a mass spectrometric analysis of the gas oil. The MS analysis essentially analyzes for various hydrocarbon group types (Cn H2n+Z) based on the hydrogen deficiency in the molecule and the results are reported based on Z numbers. Based on simple process chemistry, it is assumed that diaromatic ring structures (Z number - 12) and more highly condensed structures cannot be converted to light products and are essentially yielded as LCO and decant oil. In this report, these kind of molecules are termed refractory components. Since conversion is measured as:

$$\text{Conversion wt\%} = 100 - \text{LCO wt\%} - \text{DO wt \%}$$

The achievable conversion for any feedstock can be estimated from its hydrocarbon composition as:

Conversion wt% = 100 - refractory components wt%

This has been termed the compositional conversion constraint to indicate that conversion in excess of this value would tend to produce gas and coke rather than valuable liquid products.

Although this is a most useful concept, defining exactly which components are LCO and decant oil precursors can be challenging.

For example:

- naphthenobenzenes (z number -8) can hydrogen transfer to yield LCO rather than gasoline and thus provide an overestimate of the compositional conversion constraint,
- highly condensed napthenobenzene may be classified as diaromatic by MS and thus provide an underestimate of the compositional converion constraint.

This may be a special challenge for gas oils derived from heavy oils and bitumens which contain substantial amounts of naphthenoaromatic components.

There are two types of problematic components in FCC feedstocks:

- those components which permanently deactivate the catalyst such as nickel, vanadium and sodium,
- compounds which act as temporary poisons by neutralizing or blocking the zeolite active sites. Basic nitrogen components and heavy aromatic compounds are recognized as temporary poisons.

Whereas temporary poisons in the feedstock will significantly affect the MAT results, permanent poisons in the feedstock (metals) will have much less of an effect than in a commercial unit because of the nature of the MAT operation.

The range of gas oils used for the study include:

- IPL gas oil - a desirable conventional gas oil feed for the FCCU
- two heavy oil gas oils
- a gas oil from Suncor synthetic crude
- a shale oil
- a gas oil from the CANMET process.

Major developments in FCC catalyst technology have focussed on the development of catalyst to handle residuum and highly aromatic stocks and the development of ultrastable (USY) zeolites to improve the octane rating of catalytically cracked gasoline.

FCC catalyst are typically composed of 5-20% zeolite (faujasite) embedded in an amorphous silica alumina matrix. The major cracking activity is normally attributed to the faujasite supercage which has an internal surface area of approximately 800 m2/g and is accessed through 8-9 A° "windows".

It is thought that when cracking residuum and highly aromatic gas oils, some of the large naphthenoaromatic ring structure has restricted access to the supercage and therefore an active matrix is required to provide some cracking activity for these large molecules. Extending this reasoning, catalyst manufacturers have developed a line of residuum metals tolerant catalyst where the matrix has some of the following features:

(1) An active and selective matrix for cracking large naphthenic structures rather than allowing them to build up as coke.
(2) Large pore diameter to minimize liquid diffusional effects.
(3) Low surface area to minimize hydrocarbon entrainment and additive coke.
(4) Sinks to entrap metals.
(5) Metals and hydrothermal stability.
(6) Sacrificial acidic centres to protect zeolites from basic nitrogen components in the feedstock.

It is obviously not possible to build all the above features into one catalyst.

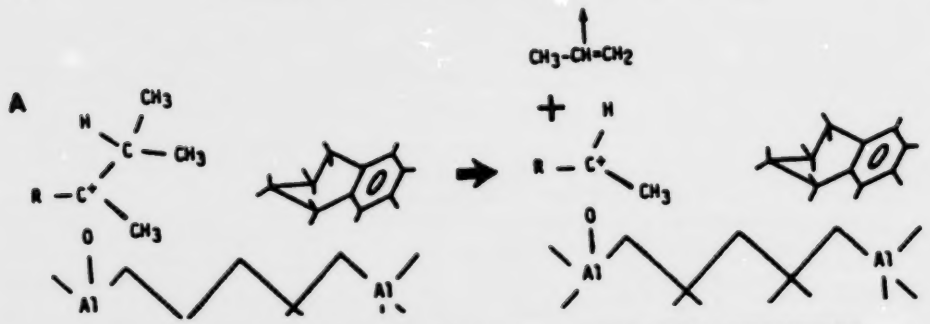
Of particular interest in this study for cracking non-conventional gas oil was a catalyst with the following features:

(1) Coke and gasoline selectivity.
(2) Ability to convert the heavy feeds at acceptable severities.
(3) Ability to resist poisoning by basic nitrogen compounds.

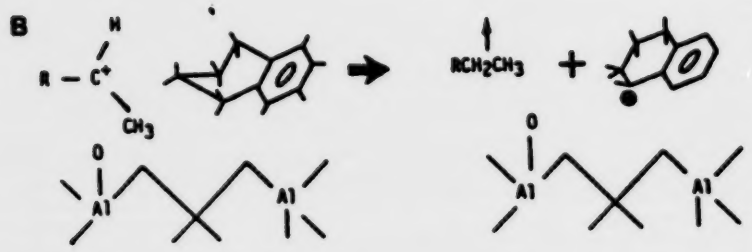
DA-440 was selected as a catalyst which may have these features.

Development of USY zeolites octane enhancing catalyst, spurred by the phase out of lead in gasoline, introduces some interesting new possiblities for catalytic cracking of feedstocks with significant naphthenoaromatic contents. These low alumina zeolites essentially increase the olefinity of the products, (and hence the octane of the gasoline) by significantly reducing the hydrogen transfer reaction. Since the alumina sites are the acidic sites responsible for both the cracking and the hydrogen transfer reaction, the reduction in alumina causes a decrease in the overall activity. In addition, it is suggested that with isolated acid sites, the cracking reactions, which produce olefins, predominate whereas for conventional REY zeolites with the more concentrated alumina sites, there is more chance of the bimolecular hydrogen transfer reaction occurring producing paraffins rather than olefins.

ISOLATED ALUMINA SITES - CRACKING



CONGESTED ALUMINA SITES - HYDROGEN TRANSFER



As shown in the above figure, the hydrogen transfer may convert naphthenoaromatic components to more condensed structures and ultimately produce coke. Thus USY catalysts, which inhibit the hydrogen transfer reaction, may be of significant benefit to cracking aromatic feedstock, in that they may encourage naphthenoaromatic to crack to gasoline and LCO rather than hydrogen transfer down to more condensed aromatic structures and yield decant oil and coke.

Nova D was selected as the octane enhancing catalyst. It contains USY zeolite and also has an active alumina based matrix.

The twin objectives for this study were:

(1) to study the catalytic cracking characteristics of non-conventional gas oils and
(2) to study the suitability of metals tolerant and octane enhancing catalyst for cracking such gas oils.

Within these objectives, it is implicitly assumed that the MAT data can be directly correlated with commercial experience. Although it is generally accepted that the yield profile from the MAT unit and commercial units show general agreement, a good theoretical framework is required to ensure that the MAT yield data is not misleading.

The MAT unit closely resembles an isothermal fixed bed reactor where WHSV, C/O ratio and reactor temperature can be independently varied. In a MAT unit, fresh feed is continuously injected into a bed of decaying catalyst and consequently the product yield profile changes with time.

The commercial riser cracker is an adiabatic dilute phase reactor. Catalyst and feedstock are injected concurrently at the base of the riser and products and catalyst are separated at the top. At steady state, the product yield profile does not change with time. The most important feature of a commercial FCCU is that it is a heat balanced operation. That is to say, the coke produced in the reactor is sufficient, when combusted in the regenerator, to provide the heat necessary to operate the unit. Because of this, the coking propensity of a particular catalyst/feedstock combination is critical in setting the C/O ratio and hence unit severity and achievable conversion. Although this contract did not include a detailed requirement for data evaluation, the MAT data has been fitted using the STA kinetic model. The results from this model were then used to aid in the interpretation of the results.

EXPERIMENTAL

The experimental work carried out under this contract included:

(1) Feedstock Characterization
(2) Catalyst Characterization
(3) Microactivity Testing (MAT).

In addition, a detailed illustration of the calcuation of the product yield structure from the MAT data is included in this section.

(1) Feedstock Characterization

The four non-conventional gas oils and the conventional VGO were characterized by a number of physical and compositional properties determined by ASTM and other generally accepted methods. The standard properties determined include: density, aniline point, viscosity, Conradson carbon content, as well as nitrogen, sulphur and metals concentrations and normal boiling range.

Densities for all the gas oils were determined in a Paar Densitometer at specific temperatures such that the material was a liquid. The density was then corrected to 15C by standard correlation tables. The densitometer measures density on the basis of an oscillating tube filled with liquid. Specific methodology is outlined in ASTM Method D4052-81. The density at 15C is converted to the specific gravity, which in turn is converted to the API gravity by the following relationship:

$$API = (141.5/s.g.\ @\ 60F) - 131.5$$

Density increases or API gravity decreases with increased residua content and/or aromatic content in a feedstock.

Aniline point is the temperature at which aniline and an equal volume of liquid hydrocarbon sample are miscible. The aniline point decreases as the aromaticity of the sample increases, assuming all factors such as molecular weight and boiling range are equal.

All feeds were analyzed for normal boiling range by a gas chromatographic simulated distillation, as described in ASTM D2887. The method consists of injecting a liquid sample into a temperature programmable gas chromatograph equipped with an 2' x 1/4" dia. 10% OV-101/Chromasorb P column and an FID

detector. The instrument is calibrated for retention time against true boiling point with a blend of n-paraffins which cover the boiling range of the sample to be determined. The instrument produces a chromatogram whose area slices are summed and normalized with respect to the total area to report a true boiling point curve for distillates on a mass % basis.

API has developed correlations which relate boiling point, API gravity and Aniline point to the Watson K factor, the carbon to hydrogen weight ratio and the molecular weight. Some caution should be exercised in using these correlations since their development was based on fractions from conventional crude oils and the distillation data is referenced to ASTM rather than simulated distillation.

The viscosity for all feeds was measured with Zeitfuch pipette at 40C and 100C, using ASTM D445.

The Conradson carbon determination is used to measure a material's propensity for forming coke. The experimental procedure employed was a modification of ASTM D189 in that an Alcor Mini Conradson carbon analyzer was used. This instrument produces superior results because it employs both a nitrogen gas blanket and an automatic programmed temperature profile. As a result, analytical data is both more precise and reproducible.

Metals analyses, particularly nickel and vanadium and sodium are another very important factor in assessing FCCU feedstocks. The nickel and vanadium are found in all crude oils, generally as porphyrin complexes. Because they are high molecular weight species they occur in the residual fractions and limit the amount of gas oil that can be drawn from the vacuum tower. Sodium is normally associated with entrained salt which would indicate poor desalter operation.

Aliquots (approx. 25 g) of the gas oils were accurately weighed into clean quartz crucibles. Dodecylbenzenesulfonic acid (0.6 g) was added and the samples were warmed for two hours on a hotplate. The hotplate temperature was increased and the samples were ignited with a torch. After combustion, the crucibles were placed in a muffle furnace (500C 3hrs) to oxidize the soot and carbonaceous residue. The ash was dissolved using a combination of hydrochloric and nitric acids. The resulting solutions were diluted to volume for metals analysis by DC plasma emission spectrophotometry.

Basic nitrogen, total nitrogen and sulphur content of gas oils are important variables in fluid catalytic cracking due to their effect on catalysts, product quality and stack gas emissions. High basic nitrogen contents in FCCU feeds are known to cause catalysts to lose activity. This has generally been attributed to the basic nitrogen compounds neutralizing the acid sites during cracking, causing the loss in activity. High sulphur contents are also deleterious to product quality, since the significant amounts of sulphur compounds contaminate FCCU liquid products. More importantly, organic sulphur and nitrogen are oxidized in the regenerator to form their respective oxides, which can present the refiner with pollution problems. Since the sulphur levels in most feedstocks are an order of magnitude greater than nitrogen levels, they present the greatest pollution problem.

The total sulphur content was determined by X-ray fluorescence according to ASTM D4292 while the total nitrogen content was determined by microcoulometry (ASTM D3431). The basic nitrogen was determined by titration using Gulf Canada Method 212.

The feedstock characterization and distillation data are given in Table 1.

The compositions of the gas oils were determined by mass spectrometry after separation by column chromatography and where necessary, distillation. For three of the samples, LHOF 12-1, LHOF 16-2 and the shale oil, the IBP was well below 300C, the minimum recommended IBP for column chromatograph procedure (GCM-302). These samples were distilled to 300C. The distillate fraction was analyzed as a light distillate by low resolution mass spectrometry according to GCM 334. While the 300C plus material was analyzed as a heavy distillate as described below.

All heavy distillate samples were separated into hydrocarbons and polars using an attapulsus clay column and the hydrocarbons separated into saturate and aromatics using an alumina/silica gel column as described by GCM-302. The saturate and aromatic fractions were then analyzed for group type by low resolution mass spectrometry (GCM-335). The various analytical data (including the analysis of the light distillate fraction, where applicable) was combined to give the analysis shown in Table 2.

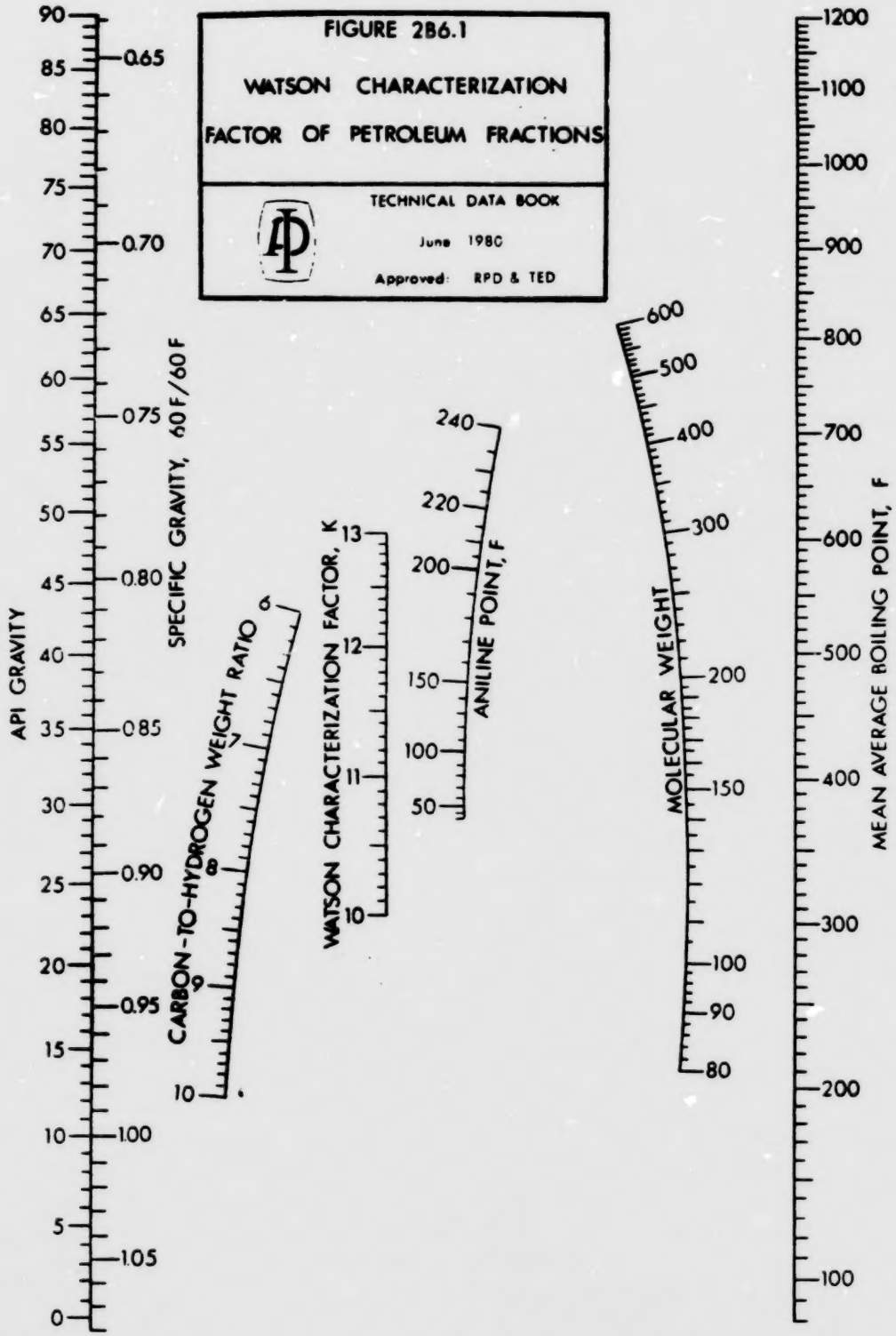


FIGURE 2B6.1

WATSON CHARACTERIZATION FACTOR OF PETROLEUM FRACTIONS

TECHNICAL DATA BOOK

June 1980

Approved: RPD & TED

(2) Catalyst Characterization

The two equilibrium catalyst samples (DA-440 and Nova D) were dried and decoked in accordance with ASTM D3907 prior to characterization. The following properties and analyses of both catalysts were determined.

1. Surface area, pore size distribution and zeolite area by N2 adsorption-desorption.

2. Surface area, pore volume and pore size distribution by mercury porosimetry.

3. Elemental analysis: V, Ni, Fe, Cu, Na, and Al.

4. Zeolite unit cell dimension.

In addition, microactivity data and physical properties were obtained from Davison Chemical

Nitrogen Sorption Measurements

The gas adsorption-desorption isotherm was obtained using the Micrometrics Orr SAPV Analyzer Model 2100. The samples were outgassed at 100C for 24 hours to remove any residual species. Nitrogen was used as the adsorbing gas. Relative pressure vs volume adsorption measurements were made over a range of relative pressures.

$$P2/P0 = 0.05 - 0.99 \text{ for Nova D}$$
$$= 0.1 - 0.99 \text{ for DA-440}$$

The BET surface area was determined by ASTM D3663. The slope and intercept of the BET diagram were used to calculate the volume of adsorbate required to complete a statistical monolayer of nitrogen and this value was converted into (nm)2 surface area by assuming a 0.162 (nm)2 cross sectional area for the nitrogen molecule.

The zeolite surface area was determined according to ASTM D4365 following the procedures described by M.F.L. Johnson. The thickness of the adsorbed nitrogen layer (t) calculated according to the equation:

$$t = \left(\frac{13.99}{0.034 - \log P2/P0} \right)^{\frac{1}{2}}$$

was plotted against the volume of nitrogen adsorbed. The surface area obtained from the slope of this plot is the mesopore area. This is subtracted from the BET surface area

to give the zeolite surface area. The micropore (zeolite) volume is obtained from the intercept of the t plot. The zeolite surface area has been correlated with the micropore volume and the percentage zeolite by M.F.L. Johnson. The nitrogen sorption measurements were also used to calculate a pore size distribution.

Mercury Porosimetry

Samples of the two catalysts were subjected to high pressure mercury intrusion using the Micrometrics Autopore 9200 porosimeter. The instrument operates on the principle that when mercury, a non-wetting liquid, is forced into a solid material the pressure required to completely fill the pores is in inverse proportion to the size of the pore . The exact relationship is given by the Washburn equation:

$$d = \frac{-4\sigma\cos\theta}{p}$$

where d is the pore diameter, σ the surface tension of mercury, θ the contact angle mercury makes with the solid and p is the pressure.

The following conditions were employed:

Mercury Contact Angle θ	: 130°
Mercury Surface Tension	: 485 dynes/cm
Pressure Range p	: 0.5-60000 psia

Since θ and σ remain constant, application of a known pressure yields the corresponding dimension.

The raw data were corrected for intrusion into the interparticle voids prior to calculating the intraparticle pore volume, the surface area and the average pore diameter. Mercury at 60,000 psia will fill 30A° pores limiting the pore volume distribution obtained by this method. Thus, this method considers only the matrix mesopores ranging from 2,400 A° to 30 A° while nitrogen adsorption ranges from the zeolite micropores to pores of 1,000 A°.

Zeolite Unit Cell Dimension

The unit cell size can be correlated with both the activity and selectivity of a gas oil cracking catalyst.

The unit cell size was determined for the two catalyst by X-ray diffraction according to ASTM. D3942. The samples were mixed with powdered silicon, and the unit cell size

calculated from the X-ray diffraction pattern of the mixture, using silicon reflections as a reference.

Elemental Analysis

Nickel, Vanadium, Iron and Aluminium were determined by X-ray spectroscopy. In summary, a dried sample was mixed with lithium tetrborate-lithium carbonate flux and fused at 1750 - 1800 F. The fusion bead was crushed, briquetted on a boric acid backing and counted in an X-ray vacuum spectrometer.

Aluminium was reported at wt% alumina (Al2O3).

Sodium and copper were determined by atomic adsorption spectroscopy and carbon using a Leco carbon analyzer.

The data obtained from the catalyst characterization is summarized in Table 3.

(3) The Microactivity Test (MAT)

A schematic drawing of the MAT unit is shown in Fig. 1. The reactor is loaded with 4.2 g of catalyst and the unit is purged with nitrogen, at temperature for at least 30 minutes before performing a test. The feed is delivered by a constant drive syringe pump through a syringe needle. On entering the reactor the feed is vaporized in the preheat zone approximately 6 cm above the bed and the vapours crack in the catalyst bed. The nitrogen purge (20ml/min) continues during and after feed injection and the run is terminated 15 minutes after start of feed injection. The weight of feed injected is determined by weighing the syringe before and after the run. Thermocouples are attached to the wall of the reactor and the thermocouple at the middle of the catalyst bed is used as the sensor for the furnace temperature controller.

The cracked products and nitrogen purge gas pass down into an ice bath cooled receiver, where the liquid products condense. The gaseous products and nitrogen purge gas pass out of the side arm of the receiver and are collected in a Ruska volumeter. The weight of liquid product is obtained by weighing the receiver before and after the run. The volume of gaseous product plus nitrogen is determined as a direct reading from the volumeter. After weighing the total liquid product, a portion is immediately pipetted into a cooled vial and the vial is then "capped" and the sample is analyzed by gas chromatographic distillation. The gas sample is discharged into an evacuated gas sample bag and the sample immediately analyzed by G.C. for (a) hydrogen and (b) all

other components. After cooling, the catalyst is removed from the reactor into a sample vial, homogenized, and submitted for a "Leco" carbon determination.

A Hewlett-Packard 5500 gas chromatograph fitted with a 2 ft x 1/4" 10% OV-101 column and a flame ionization detector is used to determine the gas chromatographic distillation (GCD). The instrument is temperature programmed from -50C to 350C and the percent distilled vs normal boiling point is automatically calculated. Calibration of elution temperature vs boiling point is done using a standard n-paraffin blend. It is most important that the elution time/b.p. calibration be maintained to ensure correct gasoline, LCO and decant oil yields. Visual inspection of the reactor effluent liquid chromatograms are used to confirm that the calibration is correct. When a small deviation is noted, the instrument is immediately recalibrated. Since there are small amounts of C4 hydrocarbon and significant amounts of C5 hydrocarbon in the liquid product, the GCD procedure is modified to calculate these components as well as a C6+ gasoline concentration. Temperatures of 216C and 343C are used as the end points for the gasoline and LCO fractions respectively. It is assumed that the weight response factor for the flame ionization detector is unity.

The major gas analysis is carried out using a Varian gas chromatograph fitted with a thermal conductivity detector and using helium as a carrier gas. The valving/column arrangement separates all the C1 - C5 paraffins and olefins, H2, N2, O2, CO, CO2, and H2S and provides an analysis of the C6+ components as a single peak.

Since the gas always contains a high concentration of nitrogen (from the purge) the chromatograph is calibrated for nitrogen on an absolute basis (known partial pressure of nitrogen at a known temperature) and the concentration of nitrogen in a gas sample is calculated directly from this calibration. This analysis is then used along with the total volume of gas collected to calculate the volume of nitrogen purge gas. This volume is then compared to the volume of nitrogen computed from the nitrogen flow rate and purge time (analytical material balance and flow material balance). With the exception of hydrogen (see below) all other component concentrations are determined using relative response factors. The response factors for this instrument are established and if necessary updated using a certified primary calibration blend from Matheson which contains nineteen hydrocarbons of interest. Separate calibration is carried out for H2S because of the reactive nature of this species. Hydrogen is determined on an absolute basis with a

chromatograph that uses a TC detector and nitrogen as the carrier gas. Hydrogen is separated from other permanent gases on a molecular sieve column while all other components are stripped to vent.

Yield Calculations

Yields are automatically computed using a IBM PC to generate the two page report shown as Tables 4 & 5. The first page contains all the input data while the second page gives component yields as weight percent (and volume percent) of feed.

To illustrate the yield calculation procedure, it is assumed that the analyses and other measurements have provided the data shown in Table 4.

With reference to the above analytical details:

- hydrogen is an absolute determination 1.3 mole % of gas sample
- nitrogen is an absolute determination 78.12 mole % of gas sample.

The other components are reported as a normalized mole percent. The mole percent of hydrocarbons plus hydrogen in the gas sample is (100-78.12) = 21.88 mole %.

The mole percent analysis is recalculated on a nitrogen free basis:

for hydrogen = 1.3 x 100/21.88 = 5.94 mole %.
for all other components e.g. methane
methane = 4.63 x (1 - 0.0594) = 4.35 mole %.

The average molecular weight for the nitrogen free portion of the gas sample is then calculated as 50.56.

The volume of the nitrogen free portion of the sample is calculated as:

394.0 x 0.2188 = 86.21 cc at 24C and 756.mm Hg
or 78.84 cc at STP.
This corresponds to 0.1778g of gas.

Grams of coke produced
= wt% coke on catalyst x wt catalyst x 1.1 x 0.01
= 0.82 x 4.2167 x 1.1 x 0.01 = 0.038g

Material balance	wt of gas	= 0.1778g	17.4 wt%
	wt of coke	= 0.0380g	3.72 wt%
	wt of liquid	= 0.8106g	79.29 wt%
		1.0264g	
	wt of feed	= 1.0223g	

Material Balance = 100.4 wt%

The effluent gas is adjusted from 17.4 wt% to 16.99 wt%. The individual gas yields are then calculated from the mole percent analysis.

$$\text{Component yield mass \%} = \frac{\text{mole \%} \times \text{molecular mass} \times \text{gas wt\%}}{\text{Gas molecular mass} \times 100}$$

For example for methane:

$$\frac{4.35 \times 16 \times 16.99}{50.56 \times 100} = 0.23 \text{ wt\%}$$

The heavy liquid yields are simply calculated from the GCD data and the overall liquid yield.

Decant oil yield = (100-85.2) x 0.7929 = 11.74 wt%

For the gasoline, C5 and C4 yields both the concentration in the gas and liquid has to be accounted for:

i-pentane in gas

$$\frac{12.63 \times (1-0.0594) \times 72.15 \times .1699}{50.56} = 2.88 \text{ wt\%}$$

i-pentane in liquid = 1.1 x 0.7929 = 0.87 wt%

Total i-pentane yield = 3.75 wt%

The liquid space velocity (WHSV) is calculated as:

$$\frac{1.0221}{45} \times \frac{3600}{4.2167} = 19.4$$

and the gas space velocity is calculated based on a feed mol.wt. of 350. The flow material balance is calculated by subtracting the total nitrogen flow (20.7 ml/min for 15 min) from the total gas volume to give a hydrocarbon volume of 83.5cc. This is equivalent to a gas weight of 0.1722g and a material balance of 99.8%.

MICROACTIVITY TEST UNIT

Fig. 1

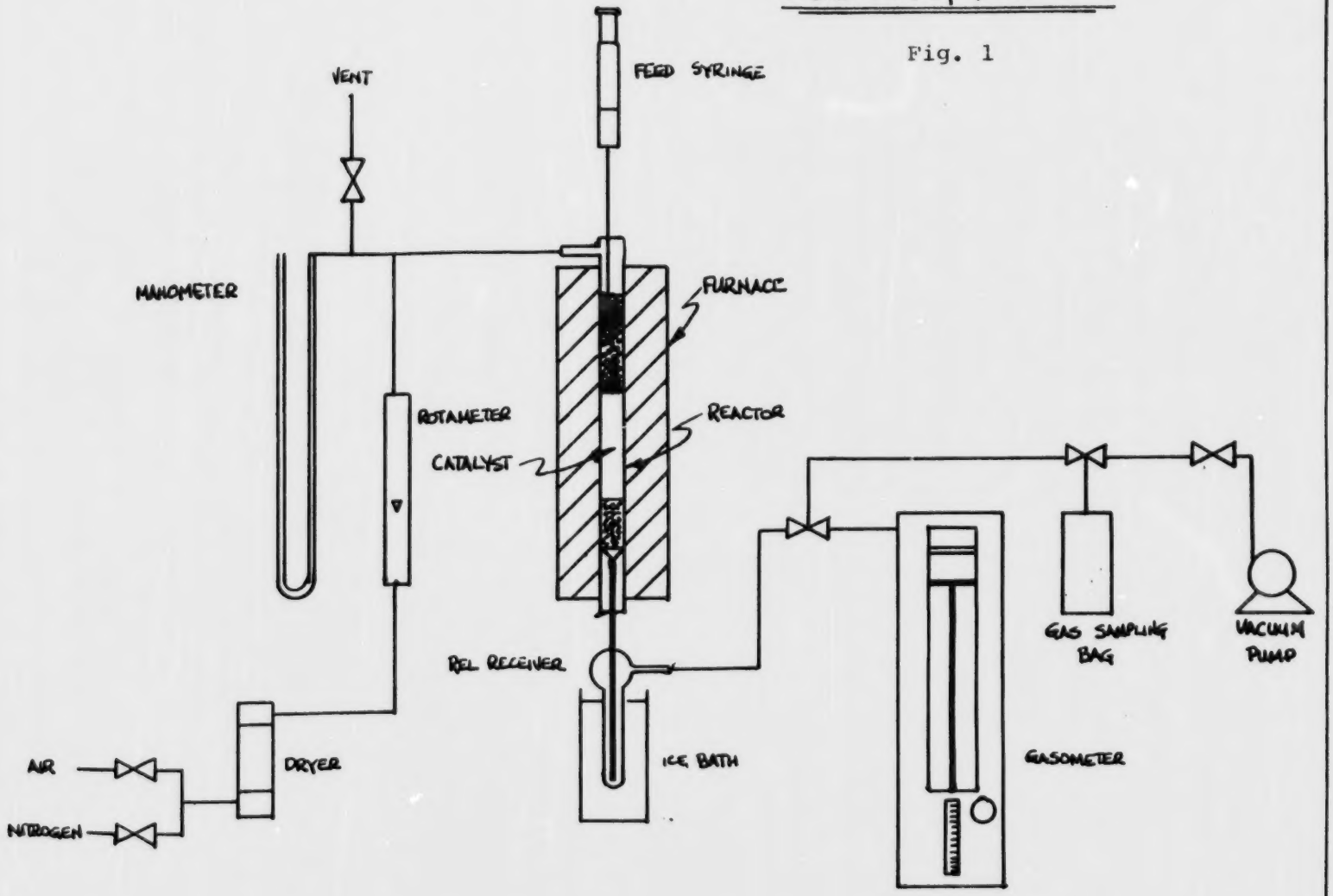


Table 4

MICROACTIVITY TEST: INPUT PARAMETERS

FILE NAME : mat43

Date of Run	87-02-17
Catalyst Type	NOVA D
Fresh Feed	SF-164
Comments	

GAS CHROMATOGRAPHIC ANALYSIS
REACTOR EFFLUENT GAS

Compound	Moles	% Feed	Compound	Moles	% Feed
Hydrogen	1.30	0.040	1-Butene	4.07	0.722
Carbon Monoxide	0.00	0.000	2-Methylpropene	1.60	0.283
Nitrogen	78.12	0.000	trans-2-Butene	4.68	0.830
Hydrogen Sulphide	0.32	0.034	cis-2-Butene	3.34	0.592
Carbon Dioxide	0.00	0.000	i-Pentane	12.63	2.880
Methane	4.63	0.235	n-Pentane	0.98	0.218
Ethane	2.98	0.282	1-Pentene	0.44	0.097
Ethylene	5.02	0.445	2-Methyl-1-Butene	0.25	0.055
Propane	6.48	0.904	trans-2-Pentene	0.92	0.205
Propene	20.03	2.665	cis-2-Pentene	1.09	0.241
i-Butane	19.63	3.606	2-Methyl-2-Butene	1.52	0.337
n-Butane	4.17	0.767	C6+	5.27	1.54

Total Moles :179.42

Molar Mass : 32.94
Hydrocarbon : 50.56

RUN CONDITIONS

Room Temperature :	24.0	Catalyst Charge g:	4.2167
Atm. Press. mmHg:	756.2	Fresh Feed g:	1.0223
Gas Volume mL:	394.0	Reactor Liquid g:	0.8106
Cat. Bed Temp. :	490.0	Injection Time s:	45.0800
Carbon on Cat. :	0.82	Feed Density g/mL:	0.9389
N2 Flow ml/min:	20.7		

REACTOR EFFLUENT LIQUID

C4 i-Paraffin :	0.040	C5 n-Paraffin :	0.220
C4 n-Paraffin :	0.020	C5 Olefin :	0.880
C4 Olefin :	0.100	IBP-216 EP :	51.500
C5 i-Paraffin :	1.100	IBP-343 EP :	85.200

Table 5

MICROACTIVITY TEST: PRODUCT YIELD STRUCTURE

FILE NAME : mat43

Date of Run 87-02-17
Catalyst Type NOVA D
Fresh Feed SF-164
Comments

PRODUCT YIELD STRUCTURE
(% Fresh Feed)

	---- YIELD ---- Mass %	Vol. %	YIELD/CONVERSION m/m	V/V
Hydrogen	0.04	0.00	0.001	0.000
Hydrogen Sulphide	0.03	0.00	0.001	0.000
Methane	0.23	0.00	0.004	0.000
Ethane	0.28	0.00	0.005	0.000
Ethylene	0.44	0.00	0.007	0.000
Propane	0.90	1.67	0.015	0.027
Propylene	2.66	4.79	0.043	0.077
i-Butane	3.64	6.07	0.059	0.097
n-Butane	0.78	1.26	0.013	0.020
C4 Olefins	2.51	3.86	0.041	0.062
i-Pentane	3.75	5.64	0.061	0.091
n-Pentane	0.39	0.58	0.006	0.009
C5 Olefins	1.63	2.34	0.027	0.037
C6+ Gasoline (216C EP)	40.51	48.77	0.658	0.782
LCO (216C-343C Cut)	26.72	26.98	0.434	0.433
Decant (343C+ Cut)	11.74	10.70	0.191	0.172
Coke Make	3.72		0.060	
REL & REG OVERALL YIELDS				
Effluent Liquid	79.29			
Effluent Gas (meas.)	17.40			
Effluent Gas (calc.)	16.99			
Conversion	61.54	62.33		

Catalyst Charge g : 4.217
Fresh Feed g : 1.022
Catalyst to Oil : 4.125
Coke on Catalyst : 0.902

Liquid SV, W/(W.hr) : 19.4
Gas SV, V/(V.sec) : 0.88

MASS BALANCE (mass% FF) :100.41 Analytical
99.86 Flow

SHERIDAN TECHNICAL ASSOCIATES INC 02-25-1987

EXPERIMENTAL DESIGN

Choice of Operating Variables

In designing a series of MAT experiments, four operating variables can be considered:

- reactor temperature
- feed injection time (on-stream time)
- catalyst/oil ratio
- weight hourly space velocity.

The last three variables are interdependant and in designing MAT runs to cover a range of severities, it is common practice to hold one of the variables constant while varying the other two. The two most common procedures are to:

(1) Vary the C/O ratio and WHSV for a constant feed injection time. To achieve this, the catalyst loading is varied over a series of experiments while the feed injection rate and time is held constant.
(2) Vary the C/O ratio and feed injection time for a constant WHSV. To achieve this, the feed injection time is varied over a series of experiments, while the feed injection rate and catalyst loading is held constant.

The MAT runs in this contract were performed at constant WHSV.

Some differences should be expected when comparing MAT yield profiles obtained when operating at constant feed injection time (on-stream time) and constant WHSV.

Coke Yield

When operating at constant on-stream time and varying the C/O ratio and WHSV for a number of experiments, then, according to Voorhies, the wt% coke deposited on the catalyst will be constant for a particular feedstock. Thus, a plot of coke as a wt% of feed vs the C/O ratio will give a straight line. The intercept will pass through zero coke for a clean feed or show positive coke if there are additive coke precursors in the feed. This approach is useful for determining additive coke values when residual feedstock are being evaluated.

When operating at constant WHSV and varying the on-stream time and C/O ratio then according to Voorhies, relationship the weight percent coke on catalyst will increase with on-

stream time.

$$\text{Wt \% Coke on catalyst} = A.t^{n}$$

where: t is the on-stream time and A and n are a function of feedstock, catalyst and temperature.

For this type of operation, a straight line should be obtained by plotting log coke vs log on-stream time. This is a more fundamental approach which allows the determination of A and n. From this the MAT coke yields can be related to coke production in the shorter on-stream time commercial operation. However, this approach does not allow the simple determination of additive coke from MAT data (and a plot of coke vs C/O ratio should not be a straight line).

Conversion

When comparing data from MAT runs obtained at constant on-stream time and constant WHSV, it is expected that the two sets of data may show some differences in the conversion vs C/O ratio plots. According to Wollaston:

$$\frac{\text{Conversion}}{\text{1-Conversion}} = k\,(C/O)^{n}\,(WHSV)^{n-1}\,\exp -AE/RT$$

where n = 0.65

When operating at constant on-stream time, an increase in the C/O ratio is accompanied by a decrease in the WHSV. Both of these changes will increase conversion.

When operating at constant WHSV, an increase in the C/O ratio is accompanied by a decrease in the on-stream time. Thus the degree of catalyst deactivation will be less at high C/O ratios again amplifying the effect of C/O on conversion. However, the WHSV and contact time effect should not be equivalent.

Kinetic Studies

If the MAT data is to be used in a kinetic model, then data should be obtained over a range of on-stream times (i.e. constant WHVS) in order to establish a catalyst decay term for the model.

The operating variables specified in the contract will provide sufficient data to evaluate various

catalyst/feedstock combinations. In addition, they will allow the use of the data in a kinetic model to obtain a more fundamental understanding of the catalytic cracking process.

Range of Operating Conditions

It is implicit in the scope of this contract that the MAT data should be interpreted in terms of commercial unit operation. It is generally accepted that MAT unit yield data approximates commercial riser caracking data. To improve the correlations, MAT unit operators have increased WHSV and reaction temperatue to obtain better correspondence. Such work is described by Campagna et al.

ASTM are evaluating a new MAT selectivity test and the conditions selected for the initial MAT runs (Milestone 4 of this contract) were closely similar to those specified in this proposed ASTM method.

Preliminary MAT Operating Conditions

C/O	Cat. Loading	Oil Injected	Injection Time	WHSV
2	4.6g	2.3g	57 sec	32 hr-1
4	4.6g	1.15g	36 sec	32 hr-1
6	4.6g	0.77g	19 sec	32 hr-1

Operating temperatures - 470C, 490C, and 510C
Nitrogen purge - 30 cc/min for 15 min from start of injection.

There were significant operating problems associated with this operation caused by the high feed injection rates and the high nitrogen purge rates. With unsieved equilibrium catalyst, the reactor pressure drop increased to 20 cm of Hg with feed injection. ASTM does not recommend operating with an inlet pressure greater than 5 cm of Hg. Such a large increase may be expected when it is realized that under these conditions the flow rate of the vapourized feed is approximately 8 ml/sec (480 ml/min) and that of the cracked products, 32 ml/sec. At such high flow rates, the calculated residence time of the feed in the bed was less than 1 sec. At such low residence times, it was suspected that small variations in residence time were affecting conversion, and producing inconsistencies in the yield data.

The high nitrogen purge rate also causes a number of problems:

- there was up to 83% nitrogen in the product gas. This reduced the sensitivity of the gas analysis and introduced the potential of significant errors in the determination of the hydrocarbon gas volume.

- at low C/O ratio the high nitrogen stripping rate was denuding the reactor effluent liquid of C6 components, increasing the error in the gasoline determination.

After discussing these problems with the Scientific Authority, it was decided to reduce the WHSV to 20 hr-1, and the nitrogen purge to 20 cc/min.

The conditions finally selected for each catalyst/feedstock combination were:

- three reactor temperatures - 470C, 490C and 510C
- for each reactor temperature:

C/O	Catalyst Loading	Oil Injected	Injection Time	WHSV
2	4.2 g	2.1 g	90 sec	20 hr-1
4	4.2 g	1.05 g	60 sec	20 hr-1
6	4.2 g	0.70 g	30 sec	20 hr-1

The yields obtained at a WHSV of 32 hr-1 are presented in Table 6.

The objective of a FCC unit operation is to maximize gasoline production within the constraints of the unit. As conversion is increased, the gasoline yield will increase to a certain point and then start to decrease as the rate of gasoline cracking exceeds the rate of gasoline production. Thus, commercial units attempt to operate at severities and convesion necessary to achieve the maximum gasoline production i.e. just below the gasoline overcracking point. Thus, it is important when evaluating feedstock/catalyst combinations on a MAT, to operate over a range of severities where conventional feedstocks show overcracking.

It was found that when operating at the above conditions, the gasoline yield from IPL gas oil decreased when the C/O ratio was increased from 4 to 6. This shows overcracking and MAT severities consistent with commercial operation.

Table 6

MICROACTIVITY TEST RESULTS USING DA-440 EQUILIBRIUM CATALYST AND IPL GAS OIL - 32 WHSV

MICROACTIVITY TEST RESULTS USING NOVA D EQUILIBRIUM CATALYST AND IPL GAS OIL - 32 WHSV

RUN NO.	13	10	14	18	17	20	26	22	25	12	11	15	19	16	21	27	23	24
Reactor TempC	470	470	470	490	490	490	510	510	510	470	470	470	490	490	490	510	510	510
WHSV HR-1	28.50	31.60	29.50	29.40	32.00	34.20	33.80	29.00	27.10	28.90	32.20	32.50	29.50	3.10	29.80	29.40	31.50	28.90
C/O	2.25	4.06	6.23	2.18	3.99	5.38	2.20	4.40	6.78	2.22	4.21	5.67	2.17	3.86	6.36	2.15	4.01	6.54
H2	0.02	0.02	0.03	0.02	0.03	0.03	0.03	0.03	0.07	0.03	0.05	0.06	0.04	0.06	0.08	0.08	0.07	0.12
H2S	0.08	0.08	0.13	0.09	0.11	0.11	0.10	0.09	0.12	0.09	0.10	0.10	0.10	0.11	0.11	0.10	0.12	0.10
C1	0.44	0.81	0.97	0.55	0.80	0.92	0.56	0.84	0.95	0.45	0.79	0.83	0.46	0.78	1.00	0.61	0.94	1.27
C2	0.20	0.38	0.40	0.27	0.45	0.48	0.36	0.46	0.48	0.20	0.33	0.36	0.28	0.40	0.46	0.32	0.45	0.51
C2-	0.28	0.49	0.58	0.32	0.53	0.64	0.42	0.59	0.70	0.24	0.42	0.51	0.31	0.49	0.61	0.36	0.54	0.72
Total Dry Gas	1.02	1.78	2.11	1.25	1.92	2.18	1.47	2.01	2.32	1.01	1.69	1.86	1.19	1.84	2.26	1.47	2.12	2.72
C3	0.68	1.31	1.47	0.74	1.40	1.69	0.93	1.31	1.59	0.61	1.09	1.31	0.71	1.23	1.47	0.78	1.22	1.55
C3-	2.28	3.18	3.20	2.42	3.33	3.49	2.90	3.51	3.89	2.35	3.31	3.54	2.85	3.73	3.86	3.01	3.82	4.49
i-C4	3.02	5.31	5.75	3.07	5.08	5.77	3.58	4.71	5.53	3.16	5.17	5.94	3.55	5.23	5.95	3.36	4.78	6.07
n-C4	0.60	1.22	1.44	0.63	1.22	1.47	0.75	1.16	1.46	0.52	0.95	1.21	0.59	1.05	1.31	0.63	1.03	1.37
C4-	2.26	3.00	2.90	2.49	3.34	3.38	3.21	3.64	3.86	2.63	3.43	3.53	3.37	4.06	4.06	3.70	4.32	4.60
Total C3C4	8.84	14.02	14.76	9.35	14.37	15.80	11.37	14.33	16.33	9.27	13.95	15.53	11.07	15.30	16.65	11.48	15.17	18.08
i-C5	3.96	4.80	6.40	3.15	5.15	5.95	4.02	5.48	6.48	3.49	5.72	6.24	4.41	5.20	6.53	3.75	4.84	7.08
n-C5	0.32	0.37	0.54	0.31	0.43	0.51	0.40	0.58	0.60	0.26	0.42	0.42	0.35	0.38	0.52	0.38	0.44	0.54
C5-	1.10	1.01	0.90	1.79	1.46	1.49	2.22	2.31	2.00	1.76	1.88	1.44	2.46	1.72	1.75	2.75	2.33	2.49
Total C5	5.38	6.18	7.84	5.25	7.04	7.95	6.64	8.37	9.08	5.51	8.02	8.10	7.22	7.30	8.80	6.88	7.61	10.11
C5-216C	44.98	47.43	46.54	43.70	48.81	48.10	43.18	48.73	48.93	43.29	50.05	47.24	46.19	48.60	47.91	43.55	46.62	50.02
C6-216C	39.60	41.25	38.70	38.45	41.77	40.15	36.54	40.36	39.85	37.78	42.03	39.14	38.97	41.30	39.11	36.67	39.01	39.91
216-343C	23.90	21.88	20.69	22.30	19.21	18.33	19.95	18.45	16.82	23.62	20.43	19.96	21.54	19.21	18.51	20.14	19.09	15.40
343C-E.P.	18.00	9.44	8.91	20.35	10.52	9.33	20.85	11.54	9.10	19.52	8.75	9.16	16.91	10.19	8.32	20.38	12.16	7.31
Coke	3.24	5.45	6.99	3.06	5.18	6.27	3.14	4.94	6.49	3.27	5.14	6.24	3.07	4.84	6.37	2.98	4.86	6.47
Conversion	58.10	68.68	70.40	57.35	70.27	72.34	59.20	70.01	74.08	56.86	70.82	70.88	61.55	70.60	73.17	59.48	68.75	77.29
Material Balance	98.10	98.20	98.00	98.30	97.50	98.40	98.90	99.20	97.70	99.00	97.70	96.90	99.70	97.80	97.40	98.60	98.50	96.90

KINETIC MODELLING OF FCCU REACTOR OPERATIONS

The following is a brief discussion of the kinetic model. A more detailed discussion is included in Appendix 1.

Significance of Model

Application of a kinetic model to the data generated during a microactivity test serves a number of purposes. It provides a rational basis for screening and evaluating MAT data in terms of consistency and significance. The kinetic parameters from the model are related directly to the basic reactions occurring during cracking thus allowing straightforward comparison of the relative rates of reaction for different catalyst-feed combinations.

This comparison can be done in terms of both the consistency of the data set as well as the significance of the data. Once the consistency of the data has been established, the kinetic parameters can be used for a range of process studies. For example, the basic kinetic parameters obtained from the MAT unit can be used in a FCC riser kinetic model to predict riser cracking yields for a particular feedstock/catalyst combination. Thus, the MAT data and associated kinetic model form the basis for a range of technical and economic studies in catalytic cracking.

Formulation of Model

The first comprehensive model, applicable to a variety of reactor configurations based on the kinetics of gas oil cracking and gasoline formation which accounts for catalyst deactivation, was developed by Weekman and Nace at Mobil R&D. This model was used to investigate the effects of different charge stock components on cracking kinetics and to correlate these effects. Ultimately, the Mobil group devised a much more complex kinetic model requiring specialized analysis of the charge stock, but capable of predicting conversion, gasoline, light fuel oil and light ends yields.

The following simplified scheme, as proposed by Weekman and Nace, is used to represent the kinetics involved in gas oil cracking.

Assuming that the overall cracking rate for gas oil is second order and that gasoline cracking is first order, the rates of formation of gas oil R(y1) and gasoline R(y2) are, respectively:

$$R(y1) = -(K_1 + K_3) \cdot y1^2 \, \phi$$

$$R(y2) = K_1 y1^2 \, \phi - K_2 y2 \, \phi$$

$$K_o = K_1 + K_3$$

where y1 and y2 are the instantaneous mole fractions of gas oil and C5+ gasoline, k are the rate constant (mole fraction/unit time) and ϕ represents the instantaneous fraction catalyst activity. The loss in catalyst activity with time, is described by:

$$d\phi/dt = -\alpha\phi , \qquad \phi = e^{-\alpha t}$$

where α is the decay rate constant and t is the on-stream time.

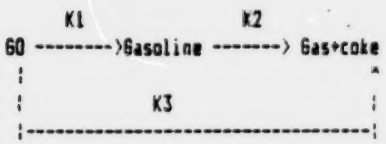
The two rate equations for the gas oil and gasoline are combined with the reactor equations, describing the configuration (fixed bed, fluidized bed, riser line) being considered, then the conversion and gasoline yield are determined by analytical or numerical integration of the resulting equations.

Application of Model

For this particular contract, the rate constants and catalyst decay constants derived from the model were used to simply check data consistency and note trends in the various kinetic parameters. The rate and catalyst decay constants are listed in Tables 7 & 8.

Table 7

SUMMARY OF WEEKMAN-NACE RATE CONSTANTS

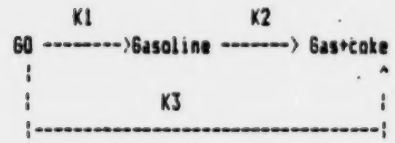


$K0 = K1 + K3$

CATALYST	FEED	TEMP DEG C	K0 hr-1	Alpha hr-1	K1 hr-1	K2 hr-1	K3 hr-1	Decay Ratio Alph/K0	Selectivity Ratio K1/K0	Cracking Ratio K2/K3	Gasoline Formation K1/K2
DA-440	Suncor	470	40.1	45.9	37.6	8.1	2.5	1.1	0.9	3.2	4.6
		490	47.7	51.8	47.5	11.8	0.2	1.1	1.0	59.0	4.0
		510	49.9	49.9	50.7	11.6	NA	1.0	1.0	NA	4.4
	Coleville	470	54.7	53.5	51.9	9.8	2.8	1.0	0.9	3.5	5.3
		490	59.6	48.3	57.6	11.3	2.0	0.8	1.0	5.7	5.1
		510	64.2	42.8	59.4	10.1	4.8	0.7	0.9	2.1	5.9
	Lloyd	470	46.7	65.5	44.3	12.2	2.4	1.4	0.9	5.1	3.6
		490	51.6	62.0	48.5	12.2	3.1	1.2	0.9	3.9	4.0
		510	53.7	62.8	48.4	11.1	5.3	1.2	0.9	2.1	4.4
	Shale Oil	470	36.3	273.1	22.4	0.0	13.9	7.5	0.6	0.0	NA
		490	29.5	195.6	18.4	0.1	11.1	6.6	0.6	.0	184.0
		510	33.3	177.8	26.3	15.6	7.0	5.3	0.8	2.2	1.7
	Canset	490	58.2	293.9	38.2	0.1	20.0	5.0	0.7	.0	382.0
		510	74.7	304.6	77.2	45.5	NA	4.1	1.0	NA	1.7
		530	62.2	236.7	50.8	22.6	11.4	3.8	0.8	2.0	2.2
	IPL	470	107.8	87.0	101.8	12.5	6.0	0.8	0.9	2.1	8.1
		490	91.7	71.8	84.2	10.6	7.5	0.8	0.9	1.4	7.9
		510	98.2	74.4	95.6	14.9	2.6	0.8	1.0	5.7	6.4

Table 8

SUMMARY OF WEEKMAN-NACE RATE CONSTANTS



KO = K1 + K3

CATALYST	FEED	TEMP DEG C	KO hr-1	Alpha hr-1	K1 hr-1	K2 hr-1	K3 hr-1	Decay Ratio Alph/KO	Selectivity Ratio K1/KO	Cracking Ratio K2/K3	Gasoline Formation K1/K2
NOVA D	Suncor	470	39.2	57.1	39.0	10.3	0.2	1.5	1.0	51.5	3.8
		490	41.9	52.8	42.3	11.6	NA	1.3	1.0	NA	3.6
		510	46.0	51.5	45.3	11.3	0.7	1.1	1.0	16.1	4.0
	Coleville	470	45.0	52.7	41.5	8.2	3.5	1.2	0.9	2.3	5.1
		490	49.5	48.7	45.8	8.9	3.7	1.0	0.9	2.4	5.1
		510	58.6	47.5	55.4	11.2	3.2	0.8	0.9	3.5	4.9
	Lloyd	470	41.1	60.2	37.7	9.6	3.4	1.5	0.9	2.8	3.9
		490	43.2	63.0	39.1	9.5	4.1	1.5	0.9	2.3	4.1
		510	46.6	65.4	42.2	11.4	4.4	1.4	0.9	2.6	3.7
	Shale Oil	470	21.0	194.2	12.9	0.8	8.1	9.2	0.6	0.1	16.1
		490	22.2	173.9	15.4	7.3	6.8	7.8	0.7	1.1	2.1
		510	22.3	144.2	15.0	5.1	7.3	6.5	0.7	0.7	2.9
	Canmet	490	50.3	319.6	32.8	0.1	17.5	6.4	0.7	.0	328.0
		510	42.6	257.2	36.4	22.6	6.2	6.0	0.9	3.6	1.6
		530	44.8	224.5	29.9	6.4	14.9	5.0	0.7	0.4	4.7
	IPL	470	109.7	104.9	100.0	11.4	9.7	1.0	0.9	1.2	8.8
		490	92.2	78.9	87.4	12.1	4.8	0.9	0.9	2.5	7.2
		510	93.6	75.0	87.8	12.7	5.8	0.8	0.9	2.2	6.9

RESULTS AND DISCUSSION

The primary purpose of this work was to evaluate the cracking characteristics of a range of non-conventional gas oils over a metals tolerant and octane enhancing catalyst. These gas oils covered a range of compositions which showed the effect of both hydrocarbon type and catalyst deactivation agents on the cracking yield profile. The discussion will review the characteristics of these gas oils and the catalysts and then will review the details of the results of the 126 MAT runs carried out under this contract, relating the data to feedstock characteristics and catalyst type.

RESULTS FROM FEEDSTOCK CHARACTERIZATION

The feedstock inspection data are given in Table 1, while the compositions are given in Table 2.

The IPL vacuum gas oil used for this contract is a typical VGO obtained from Western Canadian conventional crude oil.

This is illustrated by comparing this data with that reported by I.P. Fisher (Fuel 65 p.473, 1986) for similar material.

IPL VGO Comparison

		Present Data	Data Reported by I.P.Fisher
API		24.2	24.0
% S		0.66	0.5
% N		0.11	0.09
Conradson carbon		0.43	0.08
Ni/V ppm		0.14/0.12	-
Boiling range C 10%		369	367
50%		444	462
90%		538	555
Crackable components	wt%	75.5	75.1
Refractory	wt%	19.4	18.6
Polars and unidentified	wt%	5.1	6.3

The slightly higher heteroatom content of the present feedstock may indicate a minor difference in the source crude and/or a difference in vacuum tower operation. IPL VGO is known to be a good FCC feedstock. The compositional conversion constraint (100 - refractory components) is estimated at 80.6 wt% and these good cracking characteristics are also illustrated by its relatively high API gravity, aniline point, and characterization factor (k) when compared to the non-conventional gas oils.

The IPL VGO had a higher boiling range than the non-conventional feedstocks studied.

The Coleville gas oil, LHOF 12-1 was a 21.0 API gravity oil containing 2.22 wt% sulphur, 430 ppm nitrogen, 100 ppm basic nitrogen, 0.07 ppm vanadium and 0.06% Conradson carbon. For this study, it was classified as a relatively good feedstock with 67.7 wt% crackable components, 27.5 wt% refractory components, and a compositional conversion constraint of 72.5 wt%.

The GCD data shows that this was a light feedstock with 32 wt% of material boiling below 343C.

The Lloydminster gas oil, LHOF 16-2 was a significantly heavier oil than the Coleville oil. This 17.3 API gravity oil contained 2.86% sulphur, 920 ppm nitrogen, 250 ppm basic nitrogen, 0.01/0.008 ppm of Ni/V and 0.13% Conradson carbon. The aniline point and the characterization factor were also significantly lower, indicating a more aromatic gas oil. From the composition, it was estimated that this gas oil contains 60.3 wt% crackable components, 31.4 wt% refractory components and an estimated compositional conversion constraint of 68.6 wt%. Of particular note is the low paraffin contents of this sample (3.75%) with trends towards that expected for the gas oil fraction from bitumen rather than heavy oil. As discussed earlier, heavy oils and bitumens are thought to be biodegraded oils. The bacterial action initially removes the n-paraffins, then the i-paraffins and then other saturate hydrocarbons. The extent of biodegradation is related to the depth of the deposit, with near surface deposits being the most severely biodegraded.

The GCD data showed that this feedstock contained 25 wt% 343C minus material.

The Suncor sample SF-164 is typical of the low API gravity low sulphur gas oils produced from a synthetic crude at Fort McMurray. This 19.1 API gravity oil contained 0.24% sulphur, 0.102% total nitrogen, 110 ppm basic nitrogen and 0.15% Conradson carbon. The low basic/total nitrogen ratio along with the low wt% sulphur is typical of hydrotreated stocks. The sample had a low aniline point and characterization factor typical for aromatic gas oils. The composition indicates that there is 70.7 wt% of crackable components and 26.3 wt% of refractory components in this gas oil and an estimated compositional conversion constraint of 73.7 wt%.

The GCD data showed 20 wt% 343C minus material in this gas oil which indicates a reasonable gas oil - distillate split.

The most important characteristic of a shale oil is its basic nitrogen content. It is well accepted that nitrogen compounds poison catalytic cracking catalysts, as illustrated by a recent paper by Scherzer and MacArthur. This particular sample contains 0.715% total nitrogen and 0.457% basic nitrogen. These nitrogen compounds are normally found in the polar fraction of the gas oil. If it is assumed that there is a single nitrogen atom/polar molecule and the average molecular weight of the polar fraction is 315 then the

weight percent of nitrogen components would be:

$$\frac{0.715 \times 315}{14} = 16 \text{ wt\%}$$

This is in good agreement with the measured concentration of polar components of 15 wt%. It should be noted that there was a 5% loss on materials on the columns during the chromatographic separation (GCM 302) of the shale oil.

If it were not for the nitrogen/polar compounds, the shale oil is equivalent in composition to a conventional FCC feedstock. It has a high API gravity (25.0) and a low sulphur content (0.52%).

The M.S. analysis shows that the feed contains 65.3 wt% of crackable hydrocarbons, and 18.9% refractory aromatic structures, which would make it a most promising feedstock if the deleterious effect of the nitrogen compounds could be eliminated.

The CANMET gas oil FR #3 was not analyzed for this contract. Feedstock inspections and HRMS data provided by CANMET are included in Tables 2 and 3. This is obviously a refractory gas oil with an estimated 52.8 wt% crackable components and 47.2 wt% refractory components.

TABLE 1

Feedstocks Inspection Data

	Source		Coleville	Lloyd-minster	Suncor	IPL	
	ASTM Method	Shale Oil	LHOF 12-1	LHOF 16-2	SF-164	Vacuum Gas Oil	CANMET FR3
API		25.0	21.0	17.3	19.1	24.2	16.2
Density at 15 C	D4052	0.9035	0.9273	0.9505	0.9389	0.9082	0.9578
Aniline point, C	D611	59.1	61.0	52.1	58.4	93.7	57.5
Conradson carbon, wt%	D189	0.18	0.06	0.13	0.15	0.43	0.08
Basic nitrogen, wt%	GCM212	0.457	0.010	0.025	0.011	0.031	0.188
Total nitrogen, wt%	D3431	0.715	0.043	0.092	0.102	0.115	0.427
Total sulphur, wt%	D4294	0.52	2.22	2.86	0.24	0.66	2.24
UOP K Factor		11.7	11.4	11.2	11.3	12.0	11.0
Viscosity @ 40 C	D445	17.339	23.715	47.364	40.345		30.61
Viscosity @ 65 C						23.35	
Viscosity @ 100 C		3.563	3.971	5.509	5.099	8.49	
Ni, ppm	ORF	0.011	0.007	0.010	0.006	0.14	<0.3
V, ppm	/ICP	<0.005	0.005	0.008	<0.005	0.12	<0.3
Fe, ppm		33	0.31	0.08	1.0	1.2	<0.1
Cu, ppm		0.025	0.018	0.009	0.013	0.010	<0.1
Na, ppm		2.2	1.4	<0.5	<0.5	<0.5	<0.5
Boiling Range by GCD, C							
IBP		209	211	238	261	305	264
5%		267	258	281	300	352	298
10%		290	279	301	322	369	314
30%		349	337	356	357	410	353
50%		394	383	402	387	444	384
70%		438	430	444	423	484	416
90%		489	477	492	474	538	460
95%		506	495	508	498	561	479
FBP		536	523	543	544	594	518

TABLE 2

Feed Composition By Mass Spectrometry

	Shale Oil	Coleville LHOF 12-1	Lloyd-minster LHOF 16-2	Suncor SF-164	IPL Vacuum Gas Oil	CANMET * FR3
Paraffins	21.75	12.07	3.75	7.90	23.75	11.40
Monocycloparaffins	13.54	13.74	11.72	10.18	14.33	8.30
Condensed Cycloparaffins	13.13	26.15	24.84	28.07	24.17	17.90
Alkylbenzenes	6.93	4.51	7.36	10.48	5.74	4.80
Benzocycloparaffins	5.32	4.03	6.01	7.49	3.72	4.90
Benzodicycloparaffins	4.68	7.20	6.66	6.61	3.74	5.50
Diaromatics	11.42	11.89	15.76	15.60	9.26	20.10
Triaromatics	3.82	5.98	5.44	6.37	4.54	10.50
Tetraaromatics	1.53	2.51	2.40	2.24	2.27	4.70
Pentaaromatics	0.73	2.02	1.30	0.50	1.12	2.90
Polars	15.35	3.17	5.62	2.93	4.30	nd
Aromatic Sulphur						
2-Ring Compounds	0.78	2.43	3.47	0.26	0.75	4.80
3-Ring Compounds	0.55	2.06	2.46	1.35	1.11	3.20
4-Ring Compounds	0.05	0.58	0.52	--	0.37	1.00
Unidentified	0.42	1.66	2.69	0.02	0.84	0.00
	100.00	100.00	100.00	100.00	100.00	100.00

* Analysis provided by CANMET

CATALYST CHARACTERIZATION

Table 3 summarizes the data obtained for the two catalysts. The microactivity and particle size distributions were obtained from Davison, while the remaining information was obtained through this contract (see Experimental Section).

The microactivity data shows that the octane enhancing catalyst, Nova D, was marginally more active than the metals tolerant catalyst, DA-440, but also showed a greater coke factor and a much greater gas factor.

Microactivity Data

	Nova D	DA-440
% Conversion	72	70
Coke Factor	1.1	1.0
Gas Factor	2.4	1.1

The conditions specified by Davison Chemical to determine the % conversion are:

West Texas Gas Oil	260 - 482C
C/O ratio	2.9
WHSV	16 hr-1
Injection time	75 sec.
Reactor Temperature	482C

The surface area and pore volumes reported by Davison are in reasonable agreement with the values determined for this contract.

		Nova D	DA-440
BET Surface Area - Davison	m2/g	93	76
BET Surface Area - this study	m2/g	101.9	75.5
Pore Volume - Davison	cc/g	0.26	0.26
Pore Volume - this study	cc/g	0.266	0.245

Based on the microactivity data, the metals loading, and the physical properties, both samples were considered typical examples of equilibrium gas oil cracking catalysts.

The zeolite unit cell size, which is directly related to the silica/alumina ratio within the zeolite crystal structure, is perhaps the most important parameter in setting the performance of modern gas oil cracking catalysts. The

silica/alumina ratio governs the acid site density and distribution which ultimately affects the stability, activity and selectivity of the catalyst through regulation of the cracking and hydrogen transfer reactions.

Dealuminating the zeolite reduces the unit cell size and causes the following changes:

(1) reduces the activity of the zeolite and
(2) increases the octane rating of the cracked gasoline.

These effects have been reviewed in detail by Pine et al. In addition, it is claimed that octane enhancing catalysts improve coke selectivity.

The measured unit cell dimension for the Nova D ctalysts was 24.28 A°, while that for the DA-440 catalyst was 24.42 A°. These two values could be considered typical for equilibrium octane enhancing catalysts and conventional REY catalysts respectively. Based on these values and Davison correlations, it is estimated that the research octane of the gasoline produced when cracking over the Nova D catalyst would be 1.5 numbers greater than that produced when cracking over the DA-440 catalyst. It is also estimated that 30% more zeolite is required to be incorporated into the Nova D catalyst to match the activity of the DA-440 catalyst for conventional gas oil cracking.

The zeolite content of the Nova D and DA-440 catalyst were estimated at 10% and 7.6% respectively, based on nitrogen adsorption measurements. This is in good agreement with the requirements estimated from unit cell size. The volume of nitrogen adsorbed plotted against the thickness of the adsorbed layer (t plot) is shown in Figs. 2 & 3 for the two catalysts. The slope of the t plot is used to estimate the mesopore surface area which when subtracted from the BET surface area, gives the zeolite surface area. The zeolite content was then estimated for the zeolite surface area using data presented by Johnson.

N2 Adsorption Data

		Nova D	DA-440
BET Surface Area	m2/g	101.9	75.5
Mesopore Surface Area	m2/g	32.7	26.7
Zeolite Surface Area	m2/g	62.2	48.8
Zeolite Content	%	10.0	7.6

The nitrogen adsorption method provides data on surfaces for pore diameters of approximately 1000 A° and less. The pore size distribution within this range is given in Figs. 4 & 5 for the two catalysts.

The pore volume, surface area and pore size distribution were also determined by mercury intrusion porosimetry. This method investigates pores down to 30 A°, effectively limiting its range to the mesopore or matrix surface properties. As is shown by the similar alumina contents, see Table 3, both catalysts are designed with an active matrix to encourage bottoms cracking. Based on the porosimetry data, the Nova D catalyst has the largest matrix surface area. Since both catalysts have similar intraparticle pore volumes, the average pore diameter is less for the Nova D than DA-440 catalyst.

Mercury Intrusion Data

		Nova D	DA-440
Matrix Surface Area	m3/g	51.2	35
Intraparticle Pore Volume	cc/g	0.2658	0.2453
Average Pore Diameter	A°	208	280

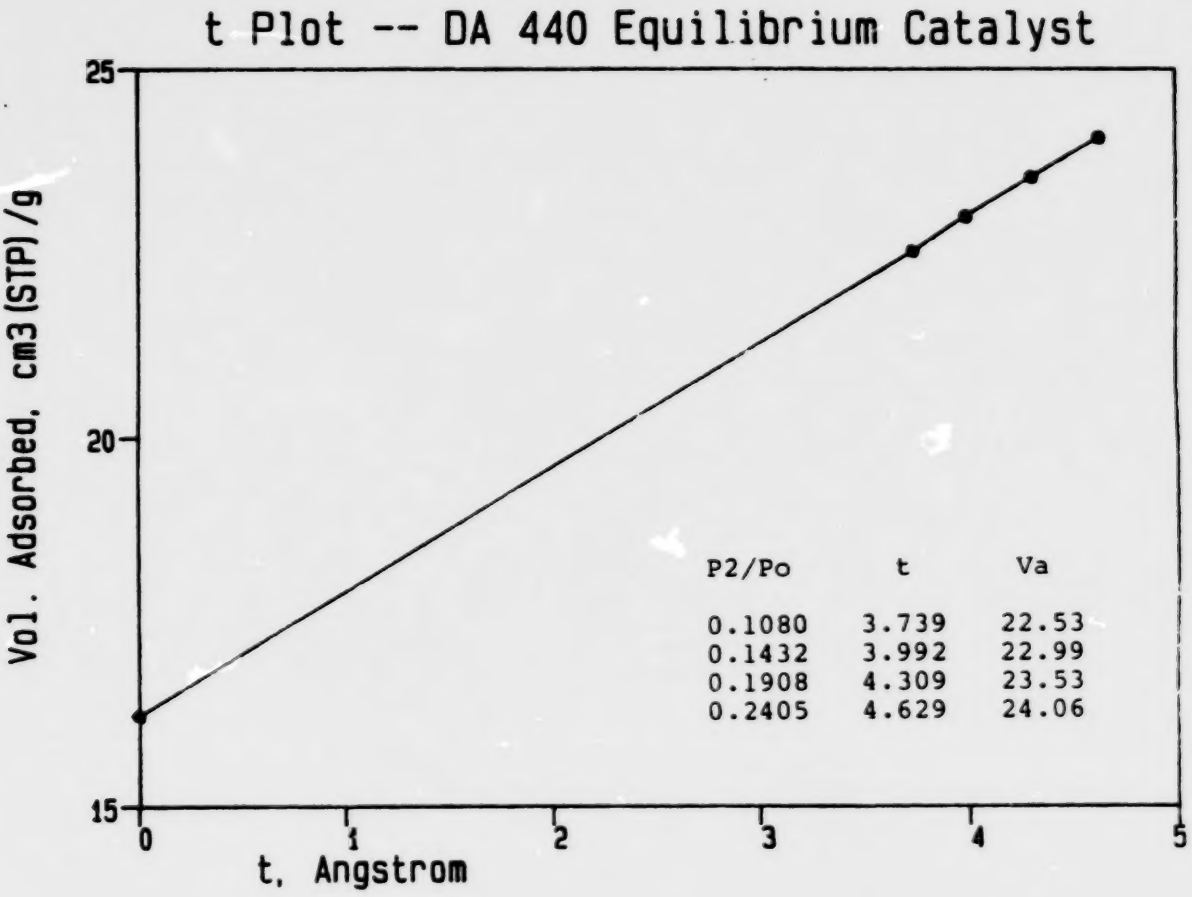
Figs. 6 & 7 show the plot of pore volume vs pore diameter for the DA-440 and Nova D catalyst respectively. In this study, any surface area effects seem to have been secondary to the large effects on activity and selectivity caused by the different unit cell size of the two catalysts.

Table 3
Equilibrium Catalyst Properties

Catalyst Source		Nova D Davison Chemical SMR 5-3332	DA-440 Canadian Refinery
N2 Adsorption Measurements			
BET surface area	m2/g	101.9	75.5
t plot surface area	m2/g	39.7	26.7
Zeolite surface area	m2/g	62.2	48.8
Micropore volume	cc/g	0.03	0.025
Zeolite content	wt%	10.0	7.6
Hg Intrusion Porosimetry to 30A°			
Surface area	m2/g	51.2	35.
Intraparticle pore volume	cc/g	0.2658	0.2453
Average pore diameter	A°	208.	280.
Elemental Analysis			
V	ppm w/w	351	141
Ni	ppm w/w	114	374
Ni+V/5	ppm w/w	185	402
Cu	ppm w/w	30	20
Fe	wt%	0.43	0.72
Na	wt%	0.15	0.34
C	wt%	0.17	0.26
Al2O3	wt%	45.3	42.1
Unit Cell Dimension A°		24.28	24.42
Physical Properties *			
Surface area	m2/g	93	76
Pore volume	cc/g	0.26	0.26
Apparent bulk density	g/cc	0.87	0.93
Particle Size Distribution	wt%		
0-20 microns		1	1
0-40 microns		16	8
0-80 microns		86	58
APS microns		59	75
Microactivity Data			
% conversion		72	70
Coke factor		1.1	1.0
Gas factor		2.4	1.1

* Davison values

Fig. 2



$$S = \frac{24.63 - 16.23}{5} = 1.68$$

$$t(\text{area}) = \frac{S \times 15.47}{0.975} = 26.66 \text{ m2/g}$$

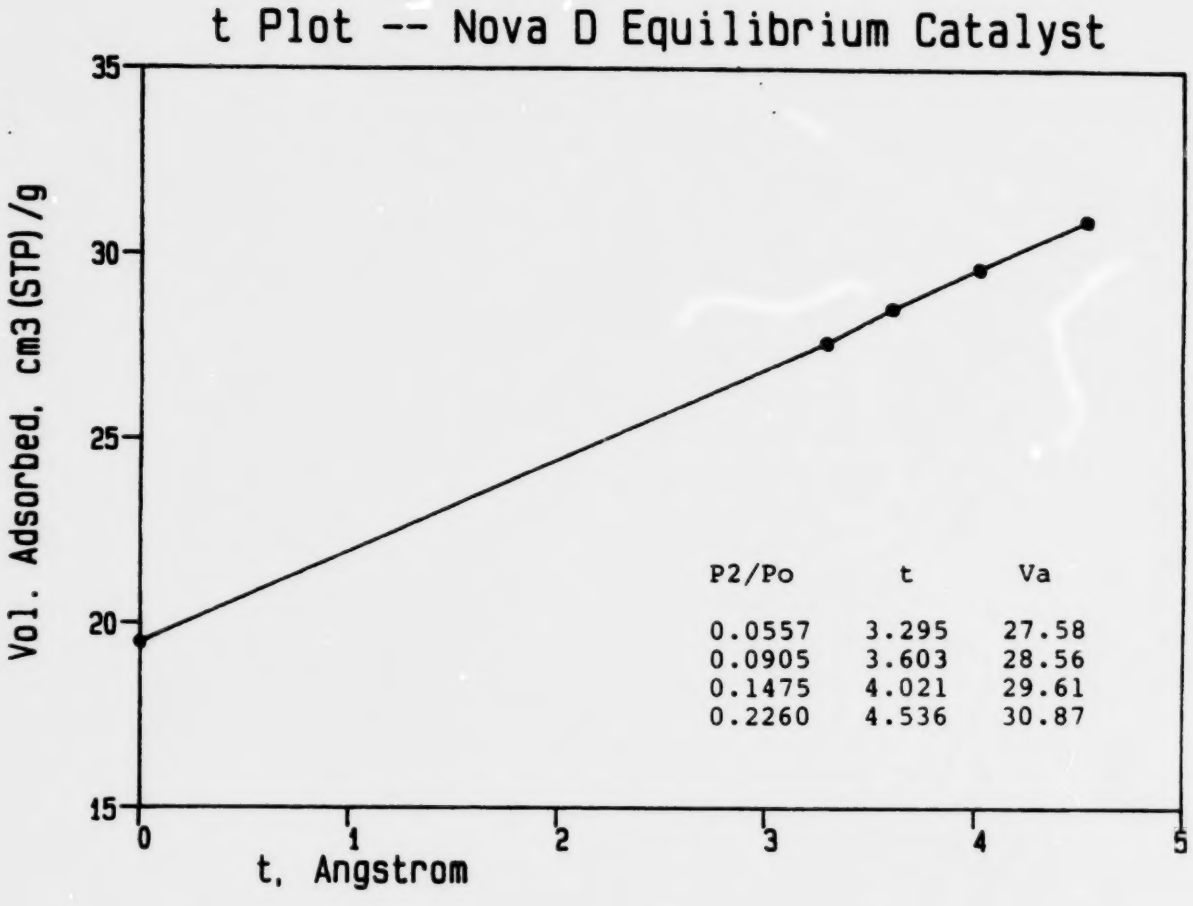
BET area = 75.5 m2/g

Micropore area = 48.8 m2/g

Micropore volume = $16.23 \times 15.47 \times 10^{-4}$ = 0.025 cc/g

From M.L.F. Johnson's plots, this micropore volume corresponds to a zeolite area of 50 m2/g and a micropore area of 48.8 m2/g corresponds to approx. 7.6% zeolite.

Fig. 3



$$S = \frac{32 - 19.5}{5} = 2.5$$

$$t(\text{area}) = \frac{S \times 15.47}{0.975} = 39.7 \text{ m2/g}$$

BET area = 101.9 m2/g

Micropore area = 62.2 m2/g

$$\text{Micropore volume} = 19.5 \times 15.47 \times 10^{-4} = 0.03 \text{ cc/g}$$

From M.L.F. Johnson's plots, this micropore volume corresponds to a zeolite area of 65 m2/g, and a micropore area of 62.2 m2/g corresponds to approx. 10% zeolite.

FIGURE 4

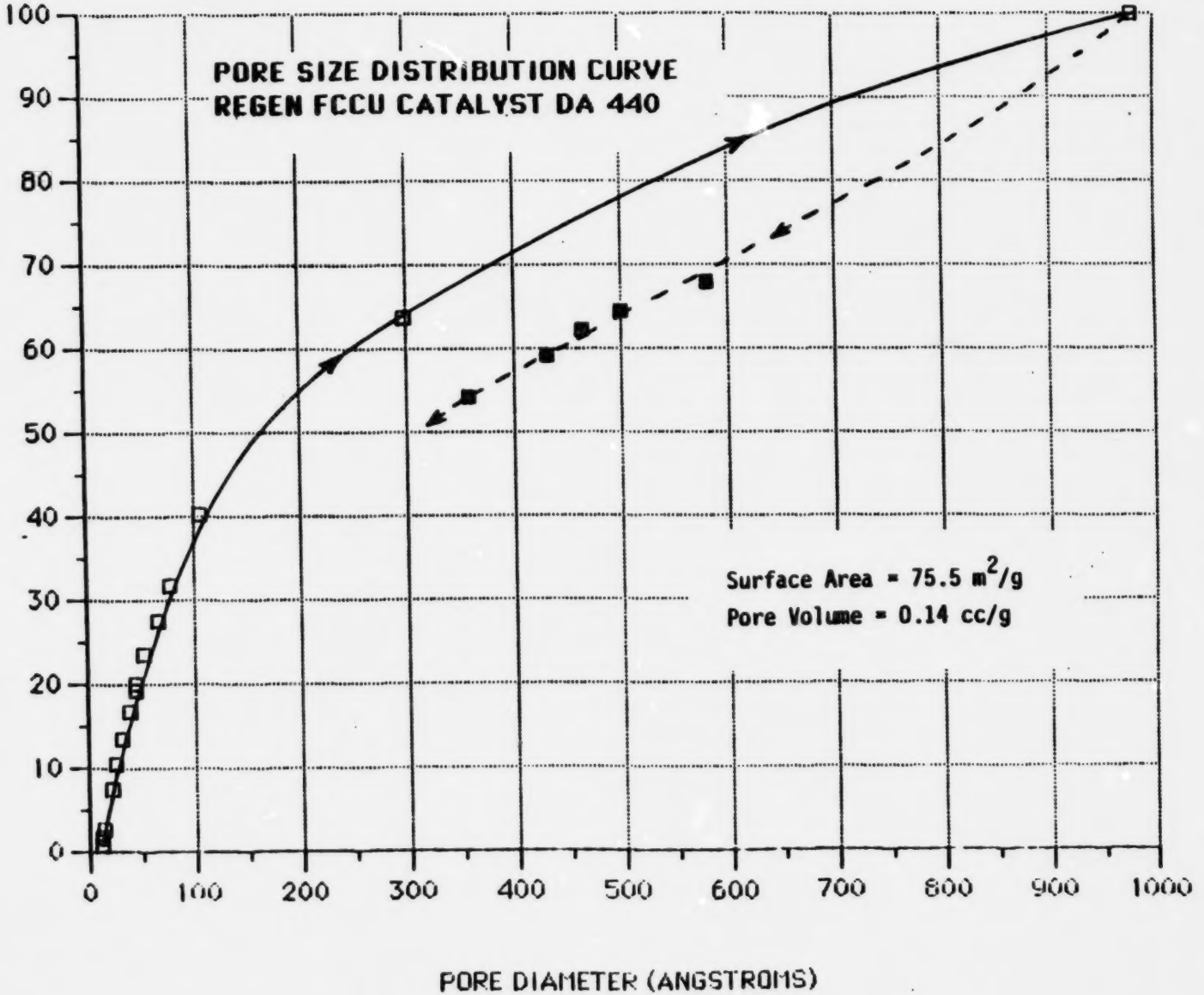

PORE SIZE DISTRIBUTION CURVE
REGEN FCCU CATALYST DA 440
Surface Area = 75.5 m²/g
Pore Volume = 0.14 cc/g
PERCENT PORES LESS THAN
PORE DIAMETER (ANGSTROMS)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIGURE 5 PORE SIZE DISTRIBUTION CURVE
REGEN FCCU CATALYST NOVA-D

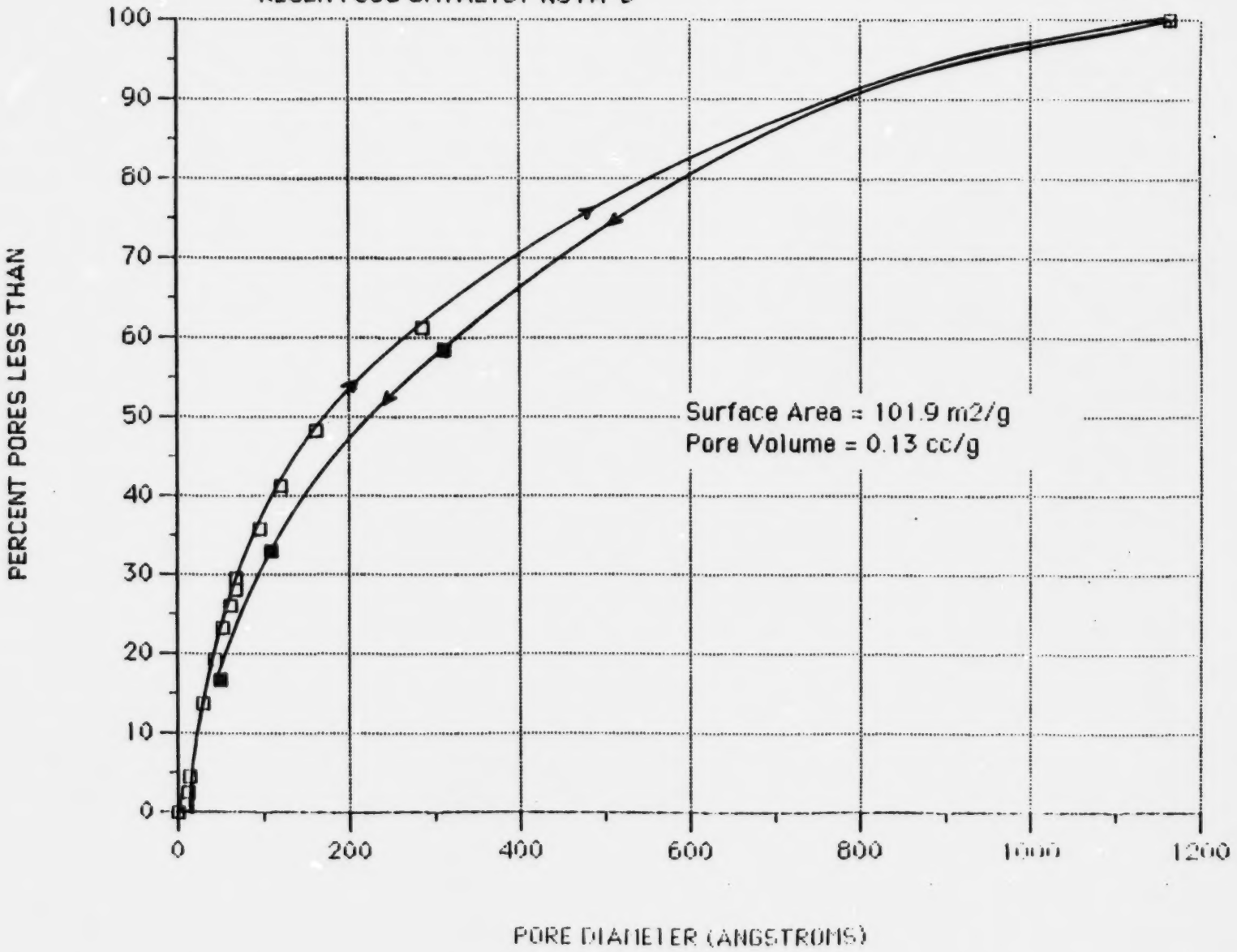


Fig. 6

MICROMERITICS AUTO-PORE 9200 V2.02

ONTARIO RESEARCH FOUNDATION, FINE PARTICLE LAB
REGEN-FCCU CATALYST DA-440, JAN 15, 87
PNTR NUMBER +613

LP 10:31:4 1/19/87
HP 10:55:55 1/19/87

CUMULATIVE PORE VOLUME (CC/G) VS. PORE DIAMETER

100% = +0.5987

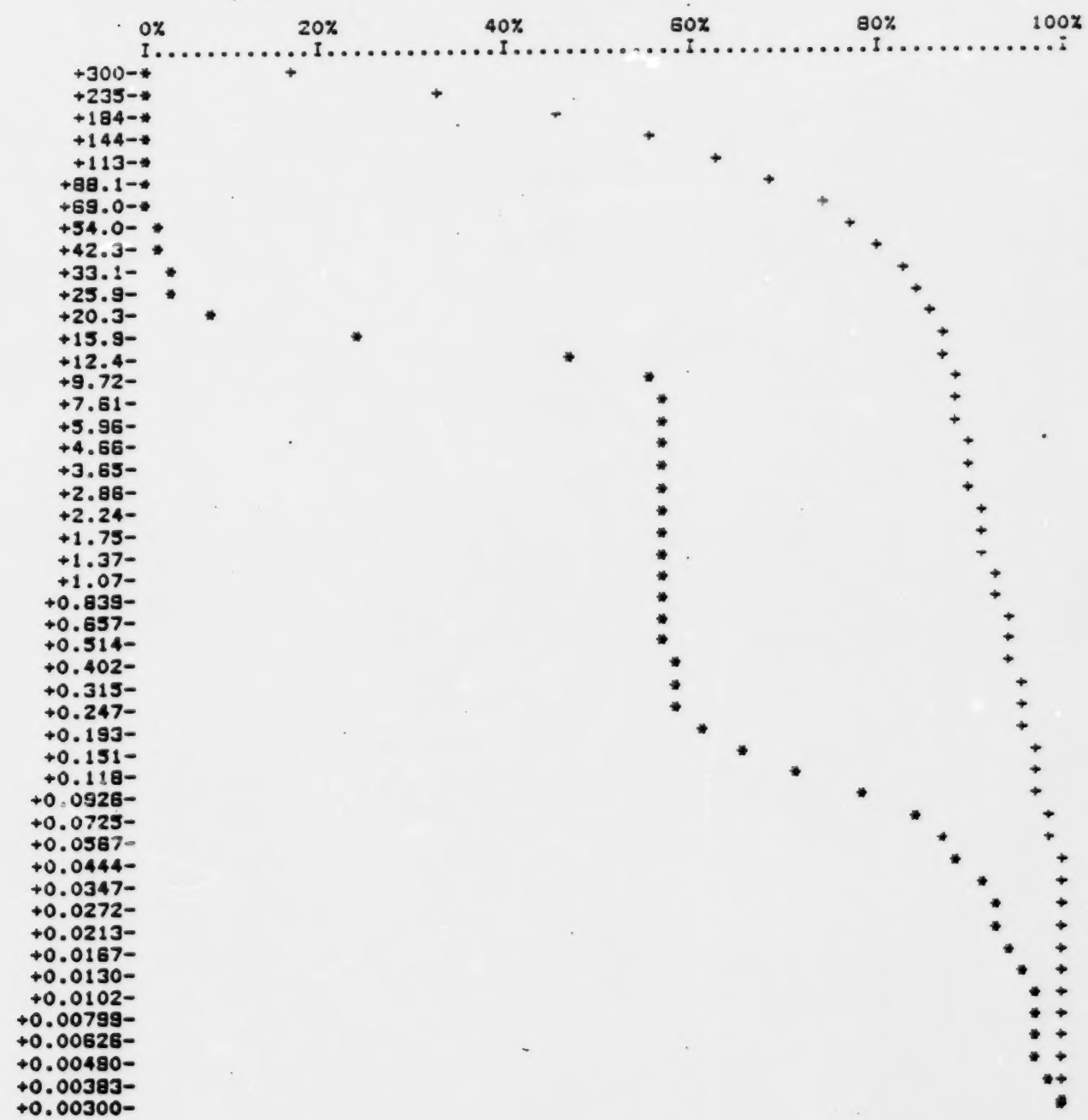


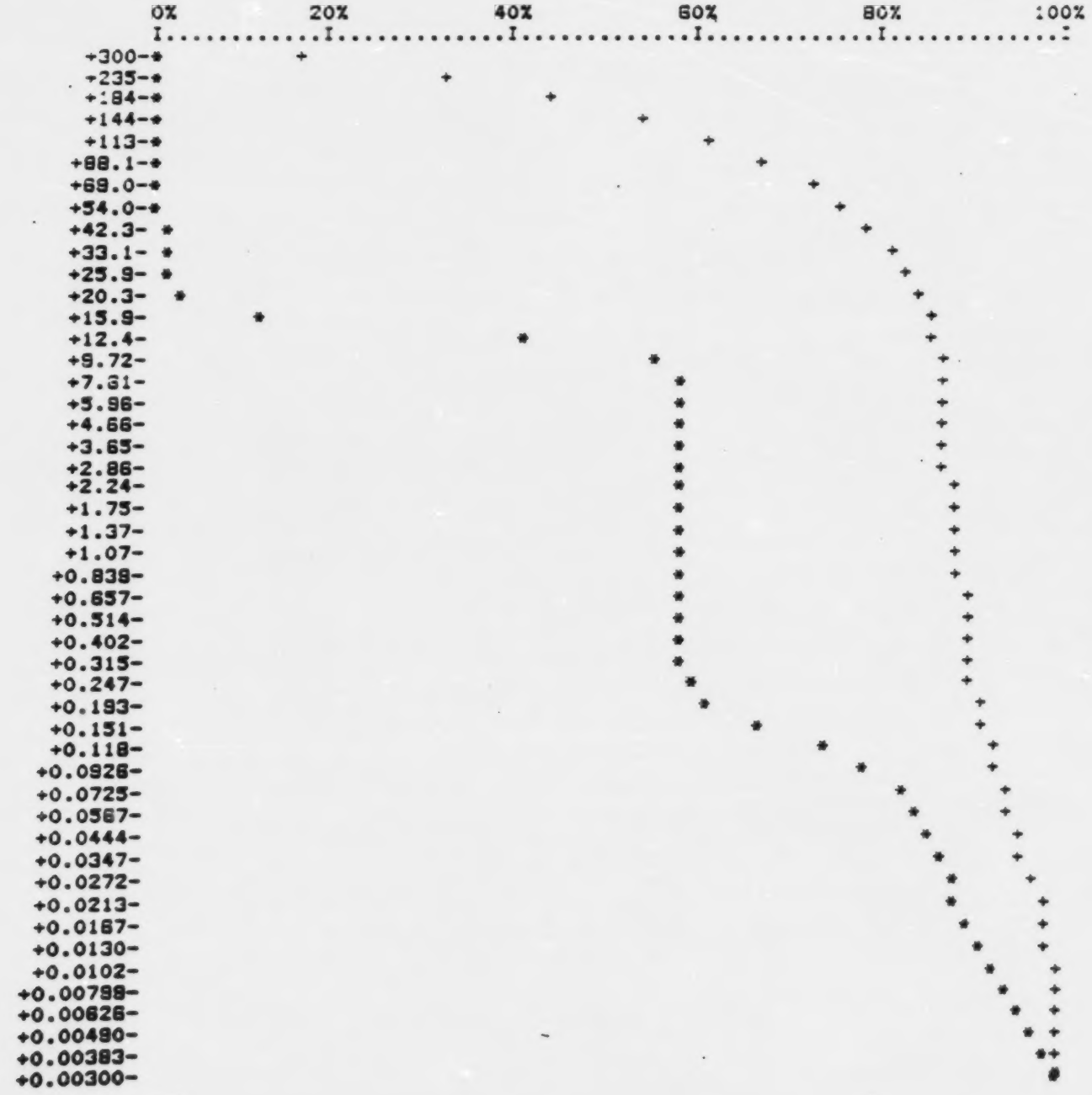
Fig. 7

MICROMERITICS AUTO-PORE 9200 V2.02

ONTARIO RESEGRCH FOUNDATION, FINE PARTICLE LAB
REGEN-FCCU CATALYST NOVA-D JAN 15/87
PNTR NUMBER +889

LP 10:31:4 1/19/87
HP 10:55:55 1/19/87

CUMULATIVE PORE VOLUME (CC/G) VS. PORE DIAMETER
100% = +0.6561



CRACKING CHARACTERISTICS OF NON-CONVENTIONAL GAS OILS OVER METALS RESISTANT AND OCTANE ENHANCING CATALYSTS

The cracking characteristics of the various gas oils will be reviewed in terms of:

(a) The compositional conversion constraint
(b) The effect of operating severity and catalyst type on feedstock conversion
(c) The effect of conversion and catalyst type on product selectivity (product selectivity plots).

The major trends in the data will first be discussed, followed by a more detailed discussion of the cracking characteristics of each individual feedstock.

Compositional Conversion Constraint

As discussed earlier, the hydrocarbon composition sets certain limits on the conversion that can be achieved with a gas oil without excessive overcracking. For non-conventional gas oils, it especially is important to establish if an optimum level of conversion is being achieved at reasonable unit severity, since they can be relatively difficult to crack.

In this report, the compositional data has been related to anticipated maximum conversion as:

Compositional Conversion Constraint = 100 - wt% refractory components.

The refractory components, i.e. components that will be yielded as either LCO or decant oil, are further defined to start at diaromatics (Z number -12) and include the more condensed aromatic structures and the aromatic sulphur components. The polar fraction is not included in the definition of refractory components. Although this is a simplification of a complex chemical process, as discussed below, it normally correlates well with maximum conversion.

Comparison of Compositional Conversion Constraint vs Measured Maximum Conversion Achieved During MAT Experiments

	Max. Observed Conversion	100 - wt% Refractory Components
IPL	79.1	80.6
Suncor	69.1	73.7
Coleville	74.0	72.5
Lloyd	69.1	68.6
Shale Oil	44.3	81.1
CANMET	54.5	52.8

Based on compositional conversion constraint, it is possible to obtain reasonable assessment of crackability of feedstocks. The major restriction to this approach was for shale oil which contains large amounts of catalyst poisons such as basic nitrogen compounds, where the high catalyst decay rate limits catalytic cracking. Processed stocks, such as the Suncor gas oil, also showed small differences between the actual measured maximum conversion and that estimated from the composition. It is surprising that the observed and predicted maximum conversion for the CANMET gas oil were closely similar considering the high nitrogen content of this gas oil.

Effect of Operating Severity and Catalyst Type on Conversion

Although the feedstock hydrocarbon composition sets achievable conversion, it is an interaction between the feedstock and catalyst that sets the severity required to achieve a reasonable conversion. For this study, the two equilibrium catalysts had similar microactivity values (72 and 70) and thus any difference in their ability to convert feedstock would indicate preferential catalyst deactivation. Gas oil conversions have been plotted against C/O ratio for the six feedstocks, with the points for each reactor temperature joined. Typically for these plots, conversion increases with C/O ratio, then at the higher C/O ratios, the conversion levels off as the system runs out of crackable components. The levelling off should correspond to the compositional conversion constraint. If the plot has not levelled off, then this is an indication that the system has not achieved optimum conversion and a more active catalyst or a more severe operating condition is required.

Both the Shale Oil and CANMET gas oils showed a straight line plot of conversion vs C/O ratio indicating severe catalyst poisoning. The Suncor gas oil data also indicated that a

more active catalyst or more severe operation would be required to achieve optimum conversion. It is thought that it may be more difficult to crack a stock such as Suncor gas oil that has already been thermally cracked. In contrast, the IPL gas oil was overcracked at the higher severity MAT conditions (C/O ratio of 6).

All the non-conventional stock achieved maximum conversion with the DA-440 catalyst, while for the IPL gas oil (and for the West Texas gas oil used in Davison's microactivity test) the Nova D catalyst provided more conversion.

Comparison of Maximum Conversion Level for DA-440 and Nova D Catalysts

Gas Oil	Max Conversion DA-440	Max Conversion Nova D	Max Rate Constant DA-440 hr-1	Max Rate Constant Nova D hr-1
IPL	77.6	79.1	107.8	109.7
Suncor	69.1	67.1	49.9	46.0
Coleville	74.0	72.6	64.2	58.6
Lloyd	69.1	66.9	53.7	46.6
Shale Oil	44.3	40.8	33.3	22.3
CANMET	54.5	49.2	58.3	44.8
Microactivity	70	72		

This effect is also shown by the difference between the calculated overall rate constant for cracking of the various gas oils over the two catalysts. This infers that the high alumina REY zeolites are more active in cracking naphthenic and naphthenoaromatic structures and also are more resistant to temporary catalyst poisons.

Product Selectivity Plots

The plot of product yield vs conversion is used to evaluate the effect of catalyst and feedstock type at constant conversion. The gasoline selectivity plots are important to determine gasoline selectivity for a particular feedstock and to establish if gasoline overcracking has occurred.

The only distinct evidence for gasoline overcracking is shown by the IPL gas oil between a C/O of 4 and 6. The Coleville, Suncor and Lloyd gas oils show a levelling off of gasoline yield with conversion but no distinct overcracking. It is not known if gasoline overcracking would be as marked with non-conventional gas oils as with more paraffinic

conventional gas oils because of the more refractory nature of the gasoline produced by cracking non-conventional oils.

The maximum gasoline yield is set by the concentration of crackable components in the feedstocks plus the severity required to achieve reasonable conversion. This is illustrated below.

	Max. Conversion Wt %	Max. Gasoline Wt %	Crackable Components Wt %	Gasoline % / Crackable
IPL	79.1	54.2	75.5	72
Suncor	69.1	47.8	70.7	68
Coleville	74.0	50.1	67.7	74
Lloyd	69.1	45.6	60.3	76
Shale Oil	44.3	27.1	65.3	41.5
CANMET	54.5	32.0	52.8	61

For the first four feedstocks, approximately 70% of the crackable components are cracked to gasoline showing a reasonably active, selective catalyst. In the case of the shale oil, the catalyst activity and selectivity is much lower showing the effect of catalyst poisoning.

The variation in predicted gasoline yield with conversion for the two catalysts is shown in Figs. 8 & 9.

Although all major product yields are plotted vs conversion, it should be noted that some yields are set mainly by the operating conditions and are only indirectly related to conversion. For example, the coke yield is set primarily by the C/O ratio and on-stream time, while the dry gas yield for all feedstocks correlates well with operating severity rather than conversion.

Fig. 8

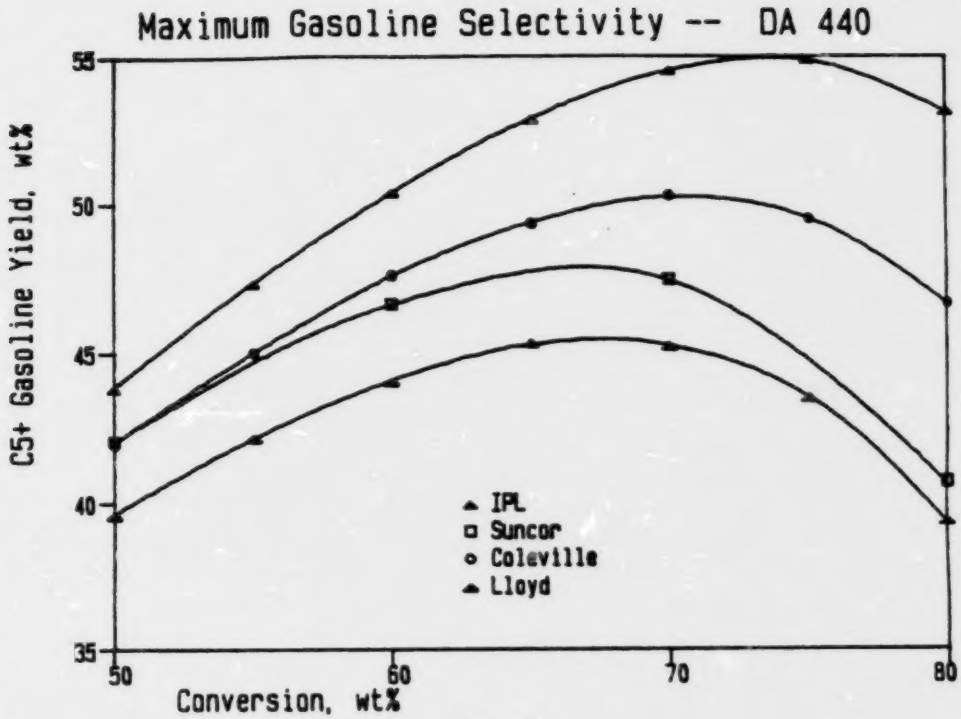
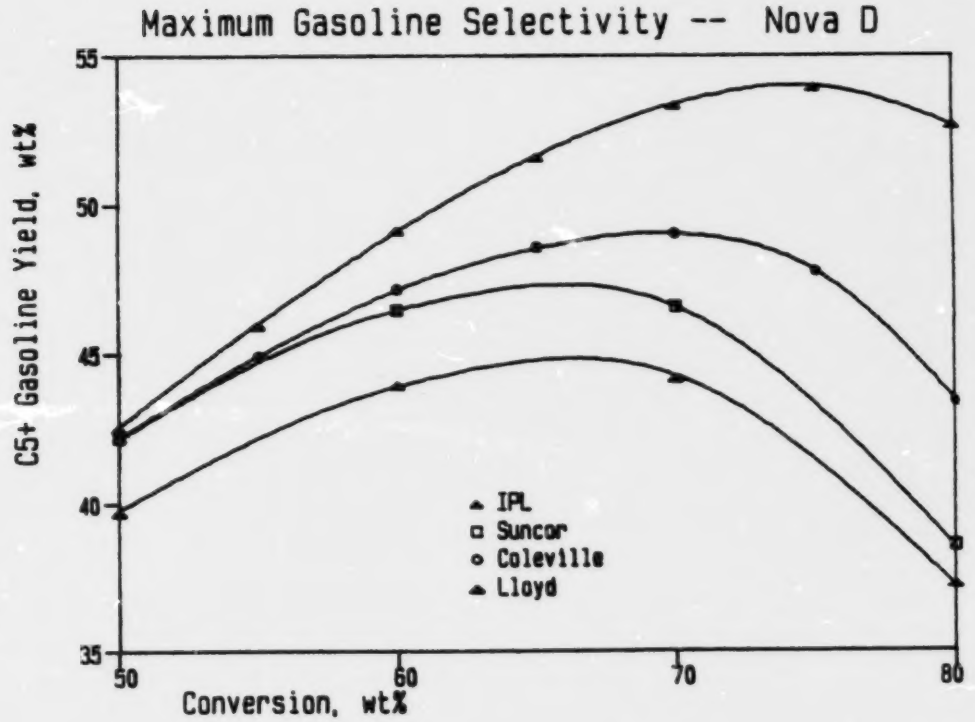

Maximum Gasoline Selectivity -- DA 440
C5+ Gasoline Yield, wt%
55
50
45
40
35
50
60
70
80
Conversion, wt%
IPL
Suncor
Coleville
Lloyd

Fig. 9


Maximum Gasoline Selectivity -- Nova D
C5+ Gasoline Yield, wt%
55
50
45
40
35
50
60
70
80
Conversion, wt%
IPL
Suncor
Coleville
Lloyd

CRACKING CHARACTERISTICS OF IPL GAS OIL

IPL gas oil was the least refractory of the feedstocks studied as would be expected from its analysis (Tables 1 & 2). It gave the highest conversion and the largest gasoline yield. This is reflected in the high rate constants for cracking and gasoline production (see Tables 7 & 8). Both the Nova D and DA-440 catalyst showed similar activity in converting IPL gas oil with Nova D giving higher conversion at high severity. This contrasts with the cracking of the non-conventional stocks, but is in agreement with the microactivity data.

Nova D	microactivity	72% conversion
DA-440	microactivity	70% conversion

There was significant gasoline overcracking for all three reactor temperatures studied, as the C/O ratio was increased from 4 to 6. This is shown in Figs. 12 & 13 where the gasoline yield is plotted against fraction converted. For this feedstock, maximum gasoline production occurs at a conversion of approximately 74%. This is in reasonable agreement with data presented by Fisher who showed maximum gasoline production for IPL VGO at 77.6%. In fact, there is good general agreement between these data and the MAT data reported by Fisher, considering that different catalysts and conditions were used.

For example, at maximum conversion:

	MAT 145	Fisher VGO C/O 5.84
H2-C2	2.81	2.0
C3C4	19.42	19.6
C5-216C	50.35	51.6
LCO	14.35	14.0
DO	6.55	6.7
Coke	6.52	6.0
Conversion	79.10	79.3

Although in these studies the two catalysts are similar in terms of conversion, the DA-440 catalyst is slightly more selective to C5+ gasoline and much more selective to C6+ gasoline production than the Nova D catalyst (see Tables 7 & 8). The two maximum gasoline cases are compared below.

	Nova D	DA-440
Run No.	155	154
Reactor Temp C	470	470
C/O	3.83	3.66
Dry Gas	1.68	1.56
C3C4	14.43	13.36
C5	8.72	8.05
C5-216C	53.36	54.24
C6-216C	44.64	46.19
LCO	17.79	18.42
DO	7.46	7.28
Coke	5.27	5.15
Conversion	74.75	74.30

Under closely similar conditions, the DA-440 catalyst yields 1.5 wt% more C6+ gasoline, while the Nova D catalyst yields 1.07 wt% more C3C4 and 0.67% more C5. This is to be expected when processing conventional feedstocks. The octane enhancing catalyst has been designed to minimize the hydrogen transfer function. Thus, production of gasoline range paraffins has been supressed in favour of the more labile olefins. Although these components enhance the octane of the gasoline, they are easier to crack than the equivalent paraffins. The above observations apply over the full range of conversions investigated during this study. The incremental C5 yields for Nova D is obvious from an inspection of Tables 7 & 8. The C3C4 yields for the two catalysts are plotted against conversion in Fig.14. For a given conversion, the C3C4 yields increases with temperature and lines are drawn through yields at equal temperatures for the two catalysts. As can be seen, the yields using Nova D for one temperature are close to the yields using DA 440 at the next higher temperature.

The dry gas yields for the two catalysts are plotted against conversion in Fig.15. As expected for a given conversion, the dry gas yield increases with reactor temperature. Again the Nova D catalyst produces marginally more dry gas.

The Nova D catalyst produces more hydrogen than the DA-440 catalyst and marginally more methane. This would be expected based on the microactivity gas factor (2.4 for Nova D vs. 1.1 for DA-440) but it is not in line with the nickel

equivalent of the two catalysts.

Comparison of Nickel Equivalents

	Ni + V/5
Nova D	184
DA-440	402

The IPL vacuum gas oil contained 3 wt% 343C minus material and the Light cycle oil yield for the 18 MAT runs ranged from 22.86 wt% to 14.35 wt%. A plot of LCO yield vs conversion (Fig.16) shows that there is a minor temperature effect. At constant conversion, the higher temperature operation will yield less LCO and more decant oil. This effect is also shown in Fig.17, a plot of decant oil yields vs conversion where at equivalent conversion an increase in temperature (decrease in C/O ratio) will increase decant oil yield. The decant oil yield shows somewhat anomalous behaviour by increasing with temperature at the high constant C/O ratios.

Variation in Decant Oil Yield with Temperature at Constant C/O Ratio

Run No.	155	149	141
C/O ratio	3.83	3.83	3.74
Reactor temp. C	470	490	510
Decant Oil Yield wt%	7.46	8.11	8.89
LCO yield wt%	17.79	17.62	16.72
C5+ gasoline yield wt%	53.36	52.35	51.88

Although the reason for an increasing decant oil yield with increasing reactor temperature is not known, it may be associated with gasoline overcracking.

The coke yield is plotted against conversion in Fig.18 with the data points for a constant reactor temperature joined to show the temperature effect. As is well known, at equivalent conversion the coke make increases as the reactor temperature is decreased. This is principally because of the need for increased C/O to maintain conversion at the lower temperature, although high operating temperatures are also thought to reduce the catalyst fouling rate. The coke vs conversion plot mirrors, to some extent, the conversion vs C/O ratio plot. For IPL gas oil, when cracked at low conversion, a small increase in the C/O ratio will cause a substantial increase in conversion but little increase in coke make. At high conversion, any further increase requires a substantial increase in the C/O ratio and hence the coke make. A review of the coke selectivity plot (Fig.18) shows that within experimental error both catalysts show equivalent coke selectivity.

Table 9

MICROACTIVITY TEST RESULTS USING
DA-440 EQUILIBRIUM CATALYST AND
IPL GAS OIL

RUN NO.	152	154	168	146	158	150	136	170	144
Reactor TempC	470	470	470	490	490	490	510	510	510
WHSV HR-1	18.60	19.60	20.20	18.80	19.10	19.50	17.50	19.40	20.20
C/O	1.92	3.66	5.30	1.90	3.76	5.49	2.04	3.67	5.37
H2	0.02	0.03	0.04	0.03	0.03	0.04	0.03	0.05	0.05
H2S	0.41	0.46	0.47	0.40	0.45	0.46	0.38	0.45	0.49
C1	0.17	0.27	0.32	0.24	0.37	0.41	0.38	0.49	0.60
C2	0.21	0.36	0.40	0.26	0.40	0.43	0.36	0.47	0.55
C2-	0.27	0.44	0.54	0.32	0.45	0.58	0.41	0.59	0.73
Total Dry Gas	1.08	1.56	1.77	1.25	1.70	1.92	1.56	2.05	2.42
C3	0.66	1.12	1.46	0.73	1.19	1.46	0.90	1.32	1.70
C3-	2.33	3.10	3.13	2.64	3.28	3.48	3.01	3.75	4.20
i-C4	3.41	5.07	5.85	3.54	4.92	5.68	3.73	5.04	6.10
n-C4	0.65	1.10	1.47	0.71	1.12	1.38	0.81	1.21	1.57
C4-	2.47	2.97	2.89	2.65	3.32	3.23	3.15	3.87	4.15
Total C3C4	9.52	13.36	14.80	10.27	13.83	15.23	11.60	13.19	17.72
i-C5	3.85	5.98	7.02	3.97	5.60	6.27	4.15	5.61	6.77
n-C5	0.39	0.43	0.54	0.42	0.50	0.48	0.52	0.49	0.58
C5-	1.72	1.64	1.01	1.90	1.70	1.68	2.36	2.09	2.16
Total C5	5.96	8.05	8.57	6.29	7.80	8.43	7.03	8.19	9.51
C5-216C	47.68	54.24	53.84	48.25	52.40	53.40	48.68	51.57	51.64
C6-216C	41.72	46.19	45.27	41.96	44.60	44.97	41.65	43.38	42.13
216-343C	22.86	18.42	16.64	21.20	18.51	16.54	19.61	17.29	15.18
343C-E.P.	15.79	7.28	6.26	16.17	8.23	6.81	15.46	9.36	7.21
Coke	3.07	5.15	6.71	2.86	5.33	6.10	3.09	4.53	5.84
Conversion	61.36	74.30	77.11	62.63	73.26	76.66	64.93	73.35	77.61
Material Balance	98.30	98.67	98.81	98.80	99.12	99.40	98.98	97.42	96.54

Table 10

MICROACTIVITY TEST RESULTS USING
NOVA D EQUILIBRIUM CATALYST AND
IPL GAS OIL

RUN NO.	153	155	161	147	149	151	139	141	145
Reactor TempC	470	470	470	490	490	490	510	510	510
WHSV HR-1	18.60	18.60	20.10	17.60	18.50	18.00	18.10	19.20	18.30
C/O	1.92	3.83	5.40	2.03	3.83	5.97	1.96	3.74	5.87
H2	0.03	0.06	0.06	0.05	0.06	0.09	0.06	0.08	0.11
H2S	0.42	0.48	0.51	0.40	0.48	0.51	0.42	0.43	0.55
C1	0.19	0.33	0.34	0.28	0.44	0.56	0.40	0.57	0.75
C2	0.22	0.36	0.39	0.27	0.40	0.53	0.36	0.46	0.63
C2-	0.26	0.45	0.51	0.30	0.49	0.66	0.38	0.53	0.77
Total Dry Gas	1.12	1.68	1.81	1.30	1.87	2.35	1.62	2.07	2.81
C3	0.64	1.15	1.34	0.70	1.18	1.65	0.82	1.27	1.81
C3-	2.35	3.34	3.50	2.82	3.69	4.04	3.23	3.94	4.71
i-C4	3.47	5.44	6.16	3.60	5.28	6.57	3.68	4.98	6.71
n-C4	0.60	1.08	1.30	0.66	1.08	1.47	0.74	1.10	1.60
C4-	2.52	3.42	3.56	3.08	3.99	3.74	3.60	4.24	4.59
Total C3C4	9.58	14.43	15.86	10.86	15.22	17.47	12.07	15.53	19.42
i-C5	3.63	6.28	7.31	3.84	5.75	6.95	3.89	5.58	7.09
n-C5	0.37	0.50	0.52	0.51	0.43	0.57	0.54	0.59	0.56
C5-	2.07	1.94	1.43	2.43	2.14	1.80	2.81	2.62	2.17
Total C5	6.07	8.72	9.26	6.80	8.32	9.32	7.24	8.79	9.82
C5-216C	43.63	53.36	52.81	48.17	52.35	52.14	47.67	51.88	50.35
C6-216C	37.56	44.64	43.55	41.37	44.03	42.82	40.43	43.09	40.53
216-343C	20.92	17.79	16.67	20.96	17.62	15.07	19.41	16.72	14.35
343C-E.P.	21.92	7.46	6.56	15.76	8.11	6.27	16.39	8.89	6.55
Coke	2.84	5.27	6.28	2.95	4.84	6.70	2.85	4.89	6.52
Conversion	57.15	74.75	76.77	63.28	74.27	78.66	64.20	74.39	79.10
Material Balance	100.18	97.91	98.53	99.53	97.75	98.39	98.92	99.57	97.71

Fig. 10 IPL & DA 440

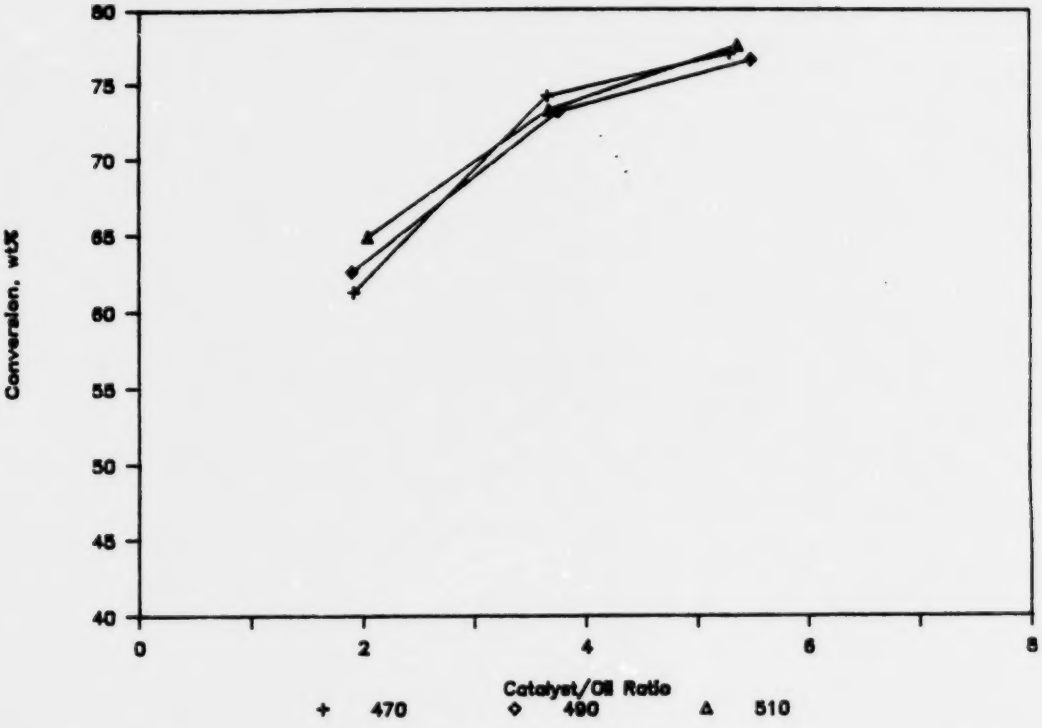


Fig. 11 IPL & Nova D

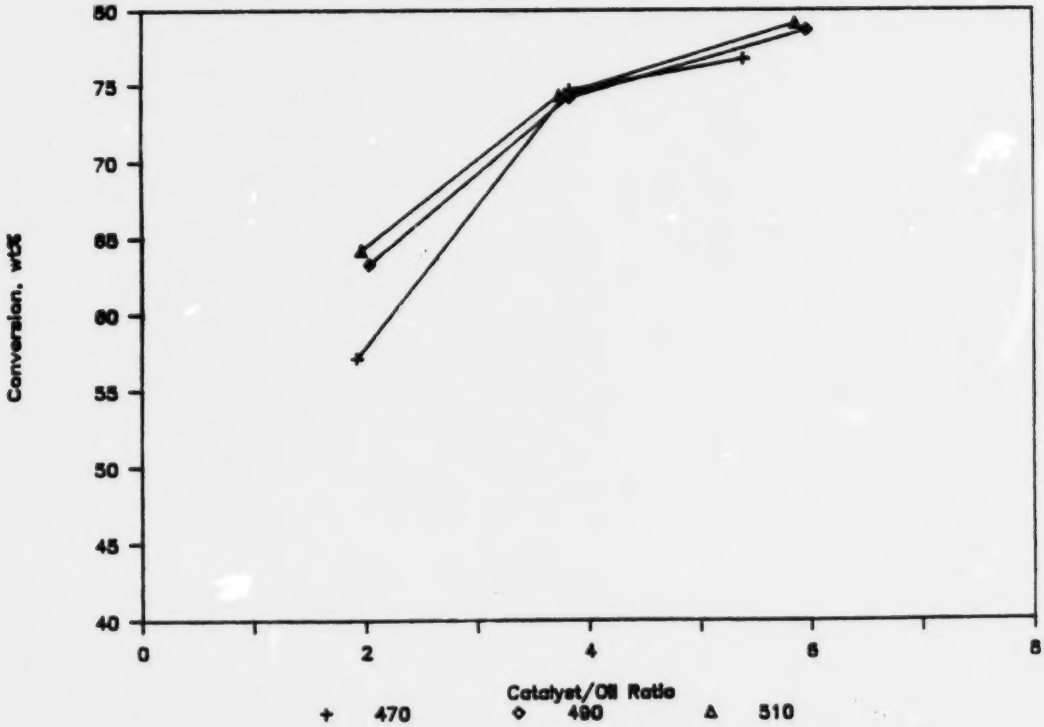


Fig. 12

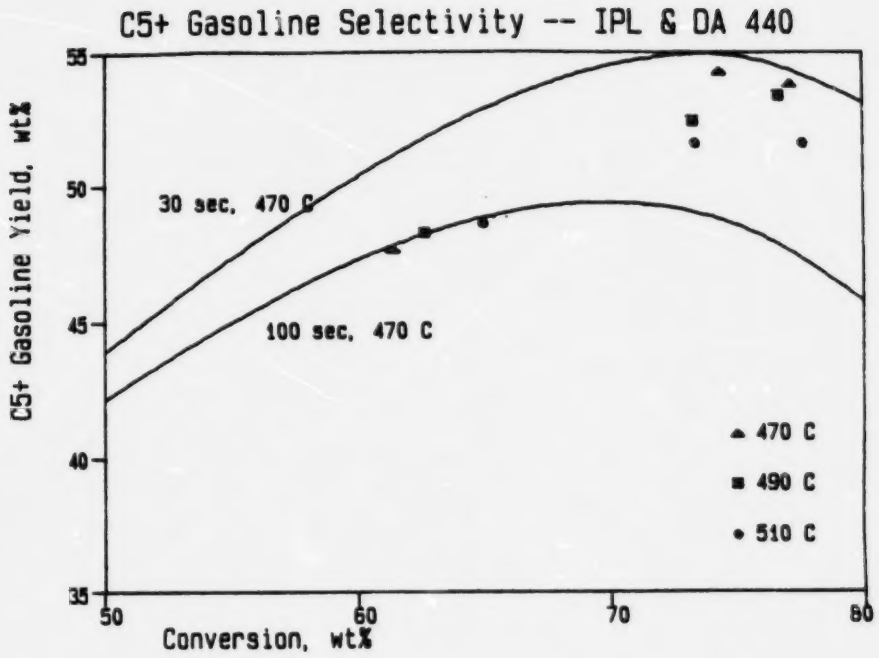

C5+ Gasoline Selectivity -- IPL & DA 440
C5+ Gasoline Yield, wt%
55
50
45
40
35
30 sec, 470 C
100 sec, 470 C
470 C
490 C
510 C
50
60
70
80
Conversion, wt%

Fig. 13

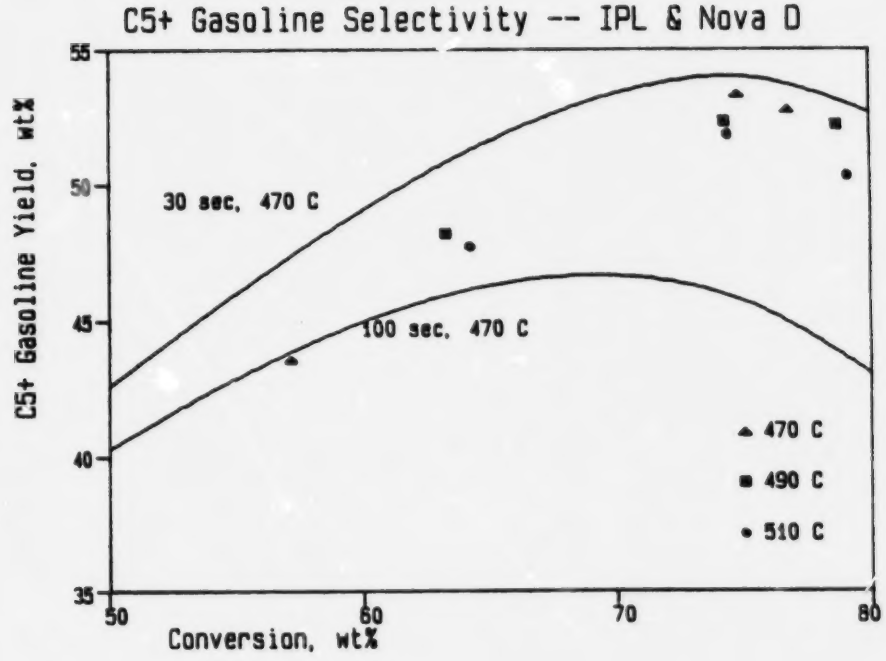

C5+ Gasoline Selectivity -- IPL & Nova D
C5+ Gasoline Yield, wt%
55
50
45
40
35
30 sec, 470 C
100 sec, 470 C
470 C
490 C
510 C
50
60
70
80
Conversion, wt%

Fig. 15 DRY GAS

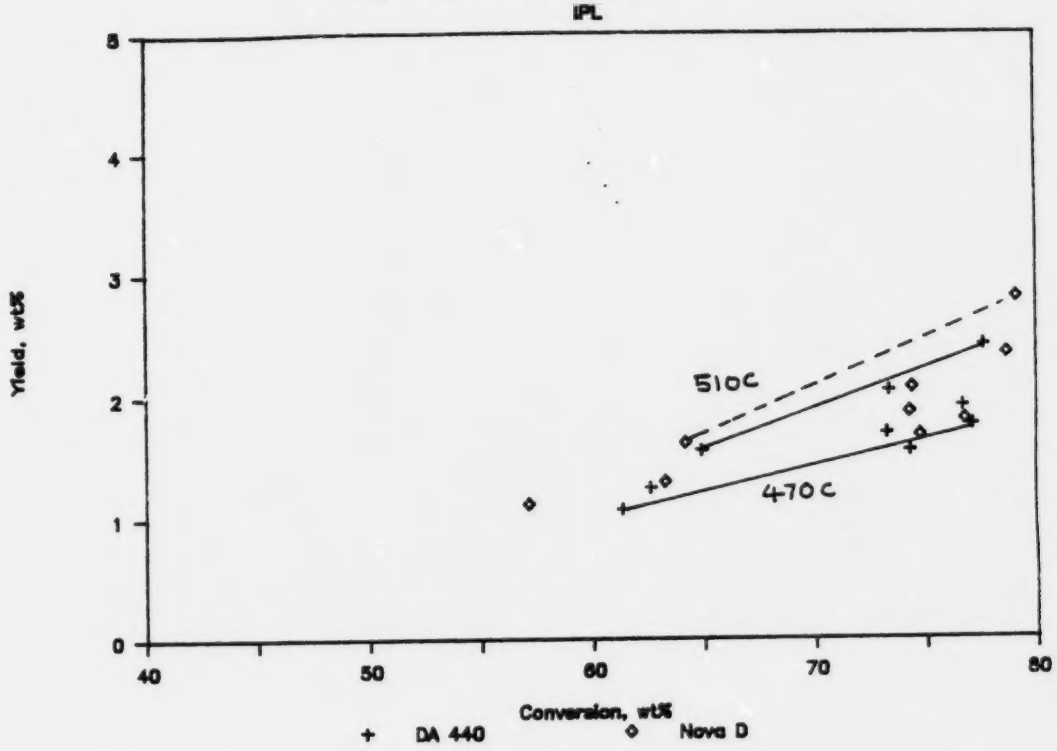


Fig. 14 C3 + C4 GAS

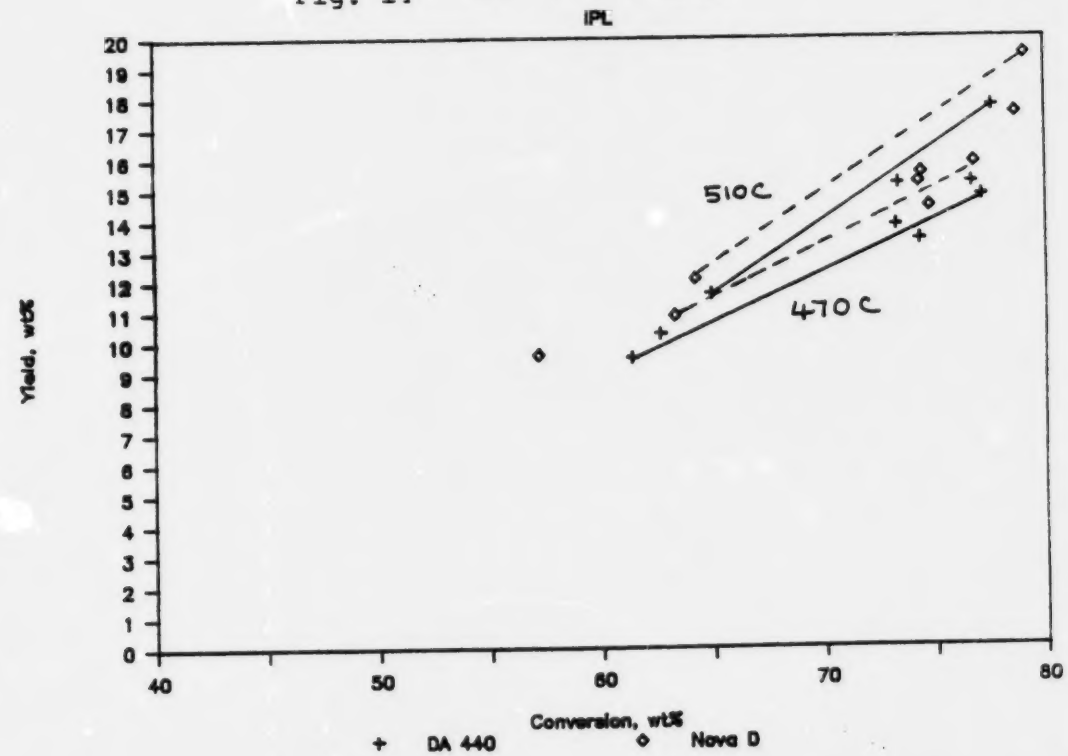


Fig. 16 CYCLE OIL

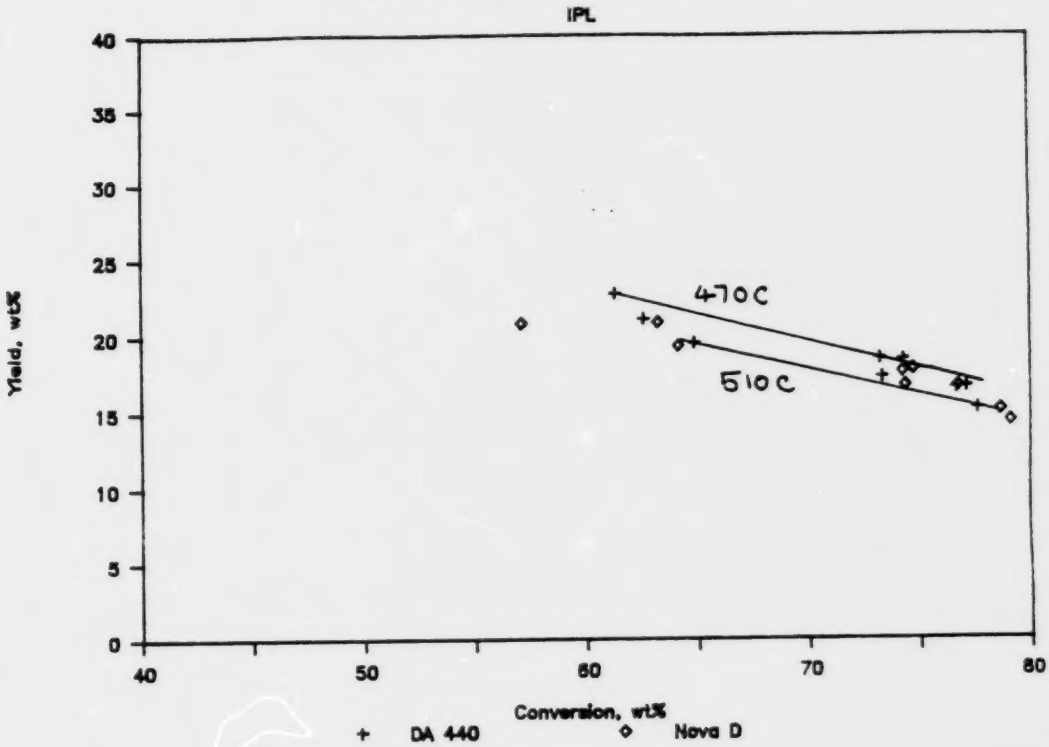


Fig. 17 DECANT OIL

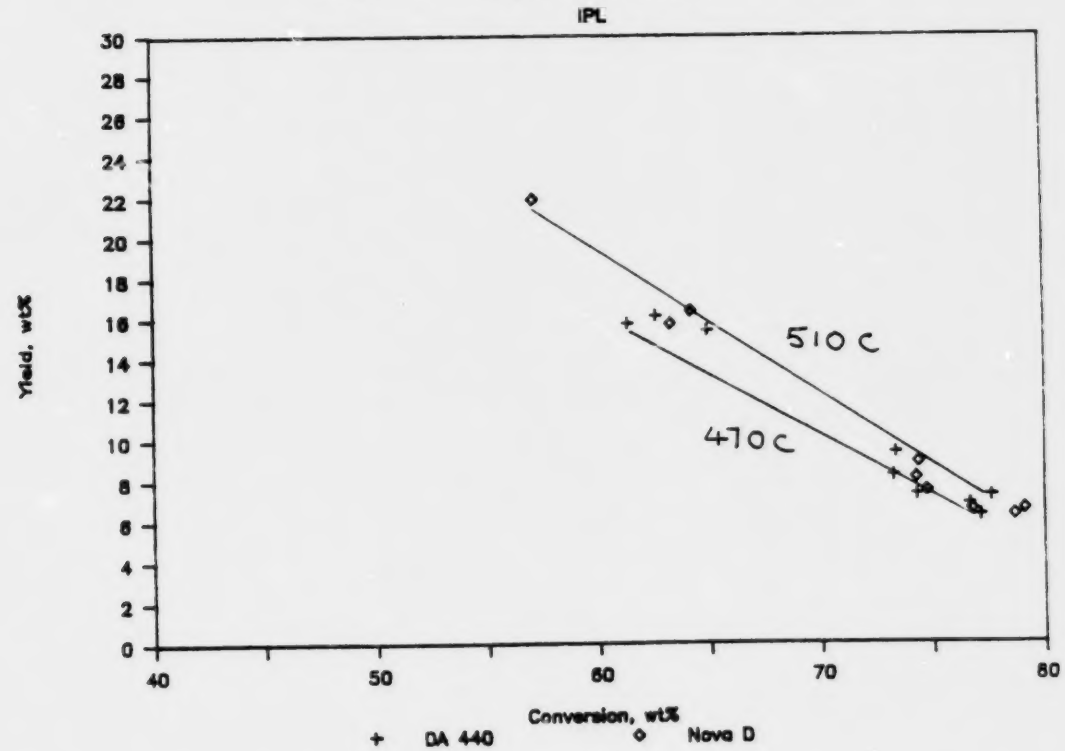
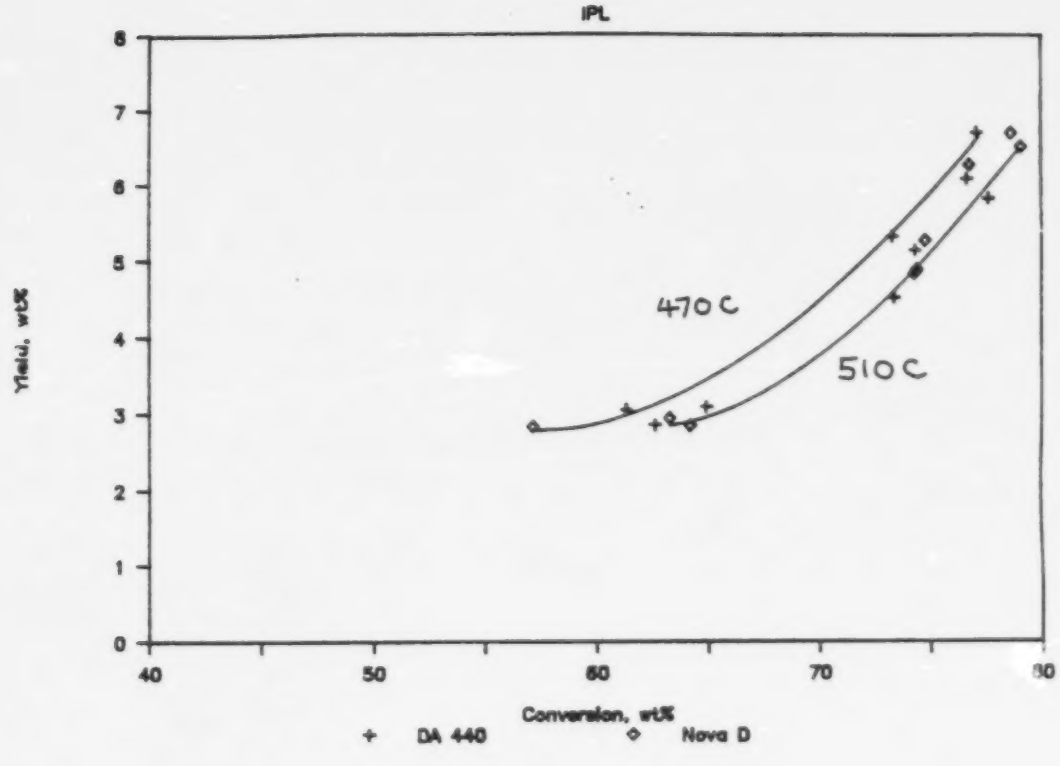
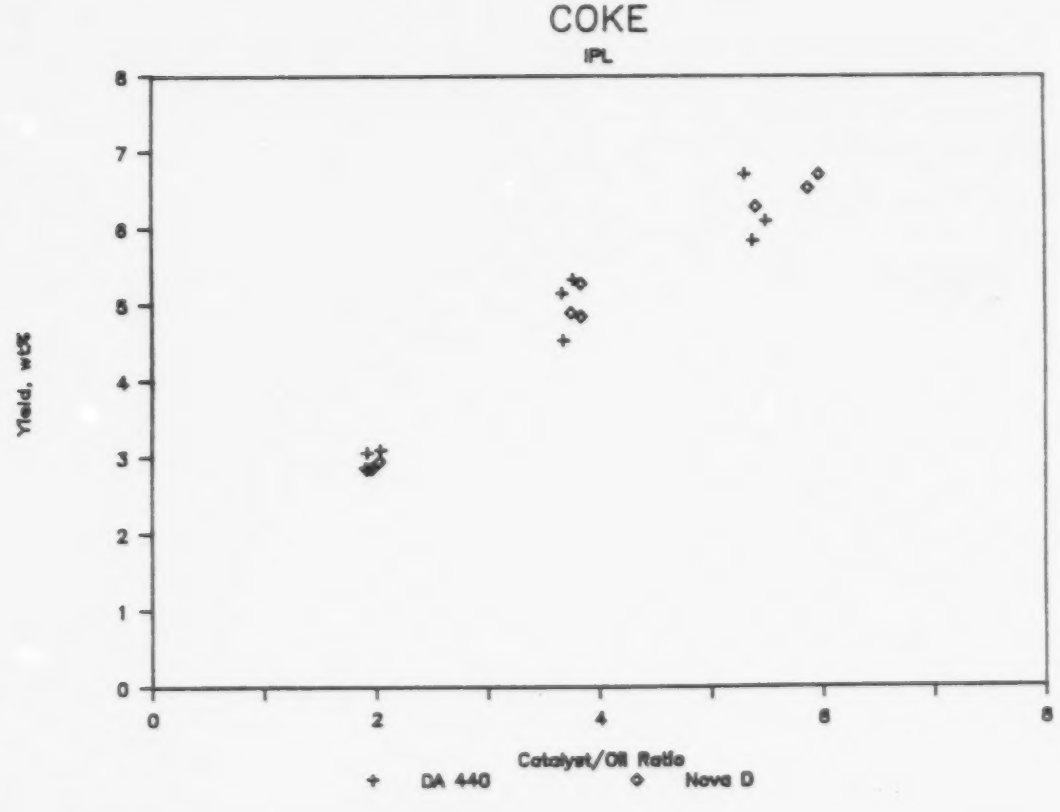


Fig. 18 COKE


IPL
Yield, wt%
470 C
510 C
Conversion, wt%
DA 440
Nova D


COKE
IPL
Yield, wt%
Catalyst/Oil Ratio
DA 440
Nova D

CRACKING CHARACTERISTICS OF COLEVILLE GAS OIL (LHOF 12-1)

Coleville was the best of the non-conventional gas oils in terms of conversion and gasoline production. This is somewhat surprising based on the compositional analysis which showed the Suncor sample SF-164 to contain more gasoline precursors and less refractory material.

Comparison of Suncor and Coleville Gas Oils

	Wt% Crackable Components	Maximum Gasoline	100 - wt% refractory components	Maximum Conversion
Suncor	70.7	47.8	73.7	69.1
Coleville	67.7	50.1	72.5	74.0

This was attributed to the fact that the Suncor sample, which had already been thermally cracked prior to hydrotreating, needed higher severity to achieve maximum conversion.

The conversion data for Coleville gas oil (Figs.19 & 20, Tables 11 & 12) shows that the DA-440 catalyst is more active than Nova D. A calculated average conversion over the nine MAT runs for the two catalysts are:

	Average Conversion
Nova D	64.9
DA-440	67.3

This is also shown by the calculated rate constant for gas oil cracking ko (see Tables 8 & 9)

	ko at 490C HR-1
Nova D	49.5
DA-440	59.6

This is in contrast to what was found for the IPL gas oil and to the reported microactivities. However, as will be discussed, all the non-conventional feeds gave higher conversions with the metals tolerant catalyst at the high severities.

The C5+ gasoline yield plotted in Figs.21 & 22 shows no sign of overcracking for either catalyst. The continuous lines of the plot from the kinetic model at a maximum and minimum gasoline operation, does predict overcracking at higher

conversions.

Overcracking of the C6+ gasoline may be occurring with the DA-440 catalyst as the C6+ gasoline yield at a C/O of 4 is marginally greater than at a C/O of 6.

DA-440 Coleville LHOF-12 C6+ Gasoline Yield

Reactor Temp.	2	4	6
470C	40.63	43.47	42.95
490C	41.86	43.13	42.90
510C	42.11	42.68	42.53

Of course, the differences between some of these data are within the expected experimental error in determining gasoline yield.

The fact that the Coleville gas oil does not show significant overcracking at conversions approximating to the compositional conversion constraint, while IPL gas oil shows overcracking at around 75% conversion which is 5 numbers below the calculated compositional conversion constraint (80.6%) is of interest. Possible explanations include:

(1) The compositional conversion constraint has been underestimated and a more severe operation is required to reach maximum gasoline and demonstrate overcracking.

(2) Feedstock deficient in paraffinic material produces a more refractory gasoline which is not as prone to overcracking as gasoline produced by cracking conventional higher paraffinic stocks.

In either case, it is possible that non-conventional gas oils would benefit from more severe conditions or more active catalyst. It is noted that Fisher reported data on cracking of hydrotreated LCO, a feedstock deficient in paraffins, where the gasoline yield increased continuously with severity, showing no signs of overcracking.

As with the IPL, the DA-440 catalyst is more selective to gasoline production. To be more precise, DA-440 produced more C5+ gasoline than Nova D at both constant severity and at constant conversion.

In terms of a constant severity case, the higher gasoline yield for DA-440 can be attributed to increased conversion.

In terms of a constant conversion case, the higher gasoline yield for DA-440 is counterbalanced by higher C3C4 and C5 yields from the Nova D operation (because of higher severity).

The plot of C3C4 yield vs conversion for the Coleville gas oil (LHOF-12) is shown in Fig. 23. For a constant conversion the C3C4 yield increases:

- as the reactor temperature is increased
- when going from DA-440 to Nova D catalyst.

These are the trends also noted for IPL.

The lines and the dotted lines on Fig. 23 show the variation in C3C4 make when cracking over DA-440 and Nova D at 510C and 470C.

It should be emphasized that at equivalent severity the C3C4 yields are closely similar for the two catalysts.

A similar trend is noted for the dry gas yield (see Fig.24) for this feedstock and two catalysts.

At constant conversion, the dry gas yield increases with temperature and Nova D produces more dry gas.

At constant severity, there is little difference between the dry gas make for the two catalysts as a weight percent of feed. However, Nova D again produces significantly more hydrogen and marginally more methane which could be a practical operating concern (wet gas compressor limitation). This feed also produces significant amounts of H2S (1.9 wt% max.) which translates to 6 lb. of sulphur/bbl of feed processed.

The Coleville gas oil contained 32 wt% of 343C minus material and the LCO yield for the 18 MAT runs ranged from a maximum of 33.19 wt% (Nova D, 470C, C/O 2.05) to a minimum of 20.67 wt% (DA 440, 510C, C/O 6.07). A plot of LCO yield vs conversion (Fig.25) is essentially a straight line for this feedstock with no apparent differentiation between the two catalysts. The above comments apply equally to the decant oil vs conversion plot which is shown in Fig.26.

Lines drawn through the set of decant oil yields (for DA-440) at 470C and 510C are almost equivalent. This is somewhat surprising since the other feedstocks having reasonable conversion show increasing decant oil with increasing temperature at constant conversion.

Again it should be noted that at equal severity, the Coleville gas oil will yield less LCO and decant oil with DA 440 than with Nova D.

The coke selectivity plot for the two catalysts is shown in Fig.27. Solid lines have been drawn through the DA-440 data and dotted lines through the Nova D data. There is a small separation between the DA-440 and the Nova D points for both the 470C and 530C plots. This could be interpreted in terms of improved coke selectivity for the DA-440 catalyst.

The spread between the coke yields at equivalent conversion for 470C and 510C is much wider than for the IPL case over the severity range studied. This is in agreement with the conversion vs C/O ratio plots which show a much greater temperature effect on conversion for the Coleville gas oil than the IPL gas oil.

Fig. 19 Coleville & DA 440

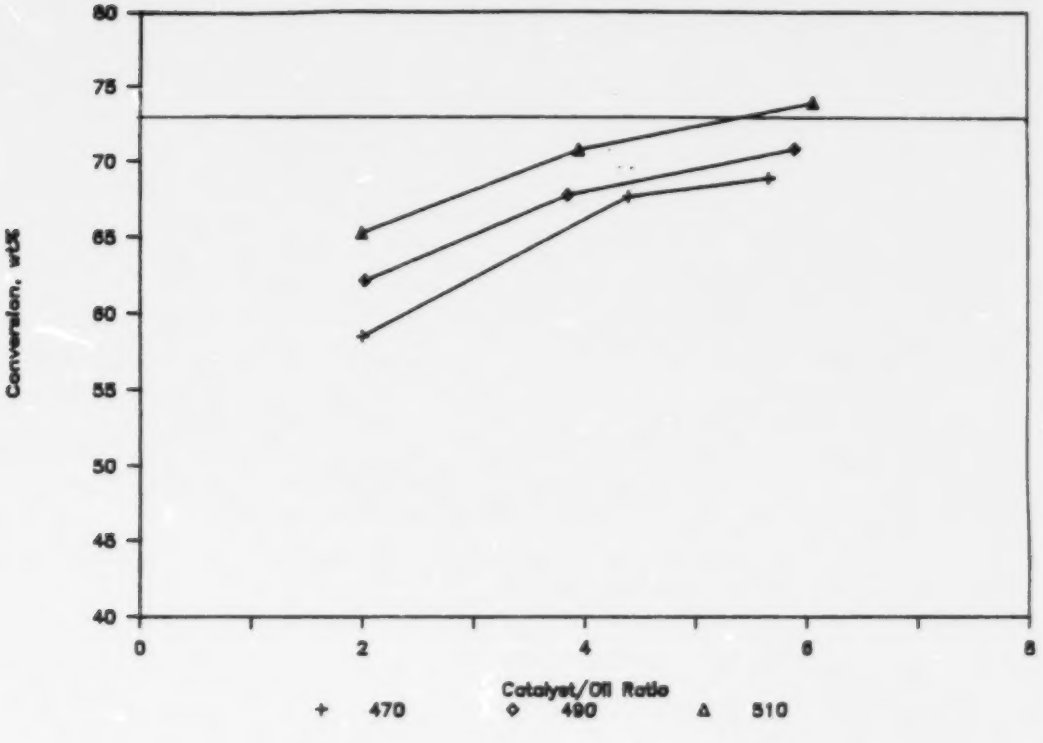


Fig. 20 Coleville & Nova D

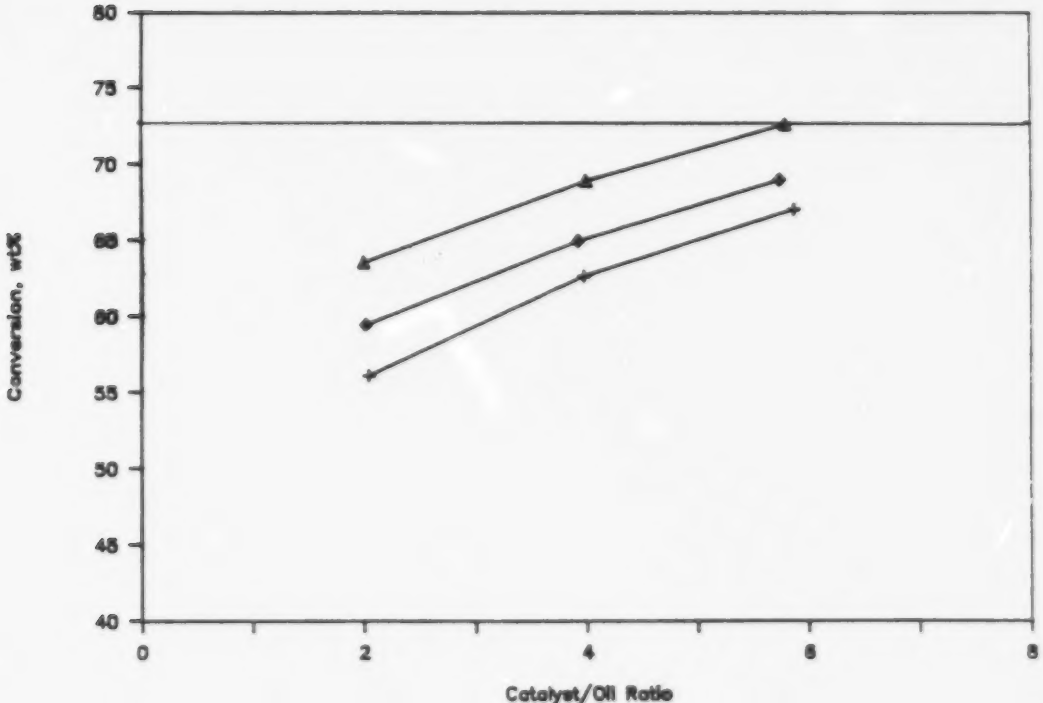


Table 11

MICROACTIVITY TEST RESULTS USING
CA 440 EQUILIBRIUM CATALYST AND
COLEVILLE GAS OIL

RUN NO.	54	56	58	60	62	64	66	68	70
Reactor TempC	470	470	470	490	490	490	510	510	510
WHSV HR-1	19.30	17.60	19.80	19.10	20.30	20.00	19.30	19.60	18.80
C/O	2.01	4.40	5.67	2.03	3.85	5.90	2.00	3.95	6.07
H2	0.01	0.03	0.03	0.03	0.03	0.02	0.02	0.03	0.03
H2S	1.55	1.76	1.73	1.65	1.68	1.79	1.69	1.77	1.81
C1	0.11	0.18	0.22	0.19	0.26	0.33	0.31	0.43	0.56
C2	0.17	0.25	0.30	0.23	0.31	0.37	0.34	0.45	0.54
C2-	0.29	0.44	0.51	0.37	0.52	0.61	0.49	0.69	0.83
Total Dry Gas	2.13	2.66	2.79	2.47	2.80	3.12	2.85	3.37	3.77
C3	0.60	1.02	1.13	0.74	0.97	1.35	0.92	1.36	1.75
C3-	2.08	2.65	2.67	2.58	2.96	3.10	3.10	3.52	3.60
i-C4	3.06	4.34	4.55	3.50	4.39	5.02	3.90	4.88	5.49
n-C4	0.57	0.92	1.02	0.67	0.93	1.18	0.80	1.12	1.42
C4-	1.94	2.32	2.37	2.44	2.70	2.71	2.92	3.08	2.91
Total C3C4	8.25	11.25	11.74	9.93	11.95	13.36	11.64	13.96	15.17
i-C5	3.44	4.65	4.92	3.87	4.72	5.33	4.26	5.21	5.76
n-C5	0.34	0.39	0.37	0.41	0.40	0.46	0.47	0.50	0.53
C5-	1.54	1.19	1.38	1.62	1.54	1.21	1.85	1.60	1.28
Total C5	5.32	6.23	6.67	5.90	6.66	7.00	6.58	7.31	7.57
C5-216C	45.95	49.70	49.62	47.76	49.79	49.90	48.69	49.99	50.10
C6-216C	40.63	43.47	42.95	41.86	43.13	42.90	42.11	42.68	42.53
216-343C	31.58	25.55	24.75	29.07	25.31	23.09	26.66	22.91	20.67
343C-E.P.	9.85	6.73	6.24	8.76	6.87	5.99	8.04	6.23	5.34
Coke	2.26	4.11	4.86	2.01	3.30	4.54	2.12	3.52	4.94
Conversion	58.58	67.72	69.01	62.17	67.83	70.92	65.30	70.86	73.99
Material Balance	99.69	99.79	99.73	98.36	98.86	98.56	98.47	98.57	99.99

Table 12

MICROACTIVITY TEST RESULTS USING
NOVA D EQUILIBRIUM CATALYST AND
COLEVILLE GAS OIL

RUN NO.	53	55	57	59	61	63	65	67	69
Reactor TempC	470	470	470	490	490	490	510	510	510
WHSV HR-1	19.10	19.40	19.20	19.30	19.70	19.90	19.30	19.30	20.10
C/O	2.05	3.98	5.87	2.02	3.93	5.74	2.00	4.00	5.79
H2	0.03	0.03	0.05	0.02	0.02	0.06	0.03	0.04	0.07
H2S	1.56	1.68	1.74	1.64	1.77	1.71	1.71	1.78	1.91
C1	0.12	0.18	0.22	0.19	0.27	0.33	0.32	0.44	0.59
C2	0.17	0.24	0.27	0.22	0.29	0.34	0.32	0.41	0.52
C2-	0.27	0.38	0.46	0.35	0.46	0.58	0.46	0.61	0.80
Total Dry Gas	2.15	2.51	2.74	2.42	2.81	3.02	2.84	3.28	3.89
C3	0.54	0.82	1.03	0.64	0.96	1.22	0.85	1.17	1.60
C3-	2.09	2.49	2.72	2.57	2.99	3.19	3.22	3.60	4.01
i-C4	3.02	3.90	4.58	3.36	4.22	4.84	3.84	4.65	5.60
n-C4	0.50	0.70	0.90	0.58	0.80	1.00	0.70	0.94	1.25
C4-	2.04	2.41	2.61	2.56	2.83	2.99	3.21	3.67	3.59
Total C3C4	8.19	10.32	11.84	9.71	11.80	13.24	11,82	14.03	16.05
i-C5	3.24	4.07	4.78	3.52	4.37	5.12	3.97	4.81	5.71
n-C5	0.35	0.38	0.39	0.41	0.42	0.42	0.49	0.49	0.54
C5-	1.61	1.53	1.54	1.87	1.64	1.67	2.24	2.06	1.95
Total C5	5.20	5.98	6.71	5.80	6.43	7.21	6.70	7.36	8.20
C5-216C	43.64	46.74	48.21	45.40	47.42	48.87	46.94	48.41	48.57
C6-216C	38.44	40.76	41.50	39.60	40.99	41.66	40.24	41.05	40.37
216-343C	33.19	29.26	26.08	31.00	27.43	24.53	27.94	24.39	21.44
343C-E.P.	10.67	8.07	6.87	9.56	7.61	6.49	8.50	6.68	5.93
Coke	2.17	3.11	4.26	1.89	2.94	3.85	1.96	3.21	4.14
Conversion	56.14	62.67	67.05	59.43	64.96	68.98	63.56	68.93	72.64
Material Balance	99.25	98.85	98.88	98.74	99.55	99.18	98.33	98.77	97.29

Fig. 24

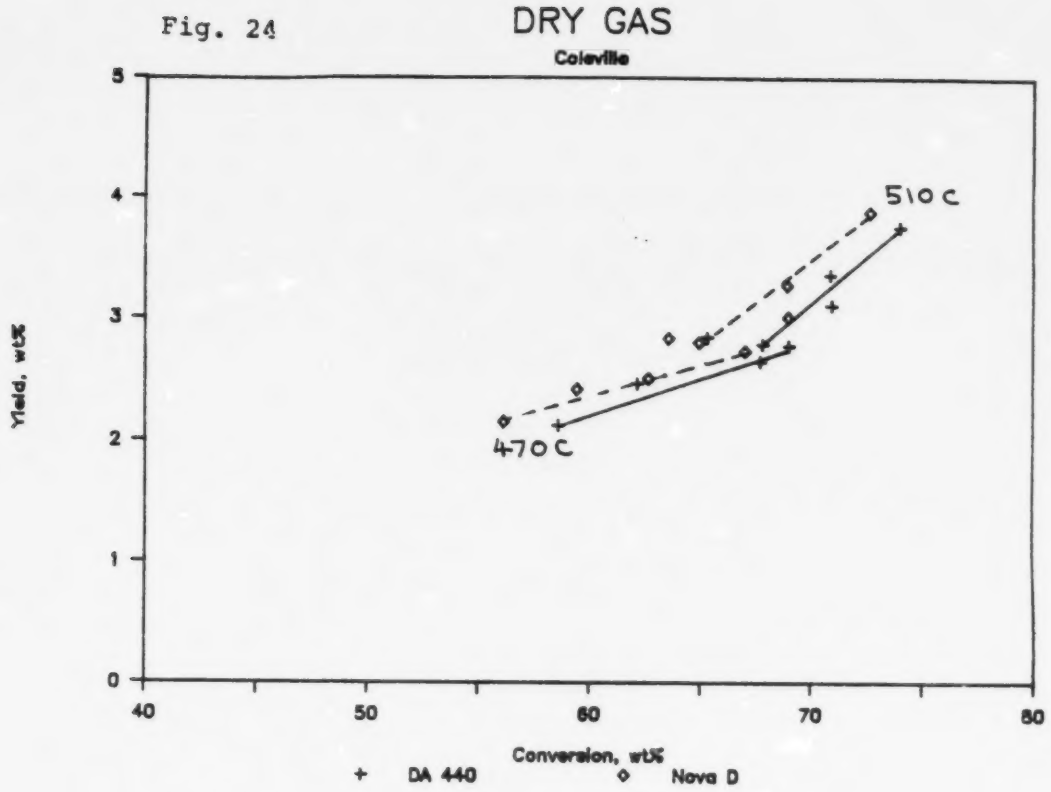

DRY GAS
Coleville
Yield, wt%
0
1
2
3
4
5
40
50
60
70
80
510 C
470 C
Conversion, wt%
+ DA 440
◇ Nova D

Fig. 23

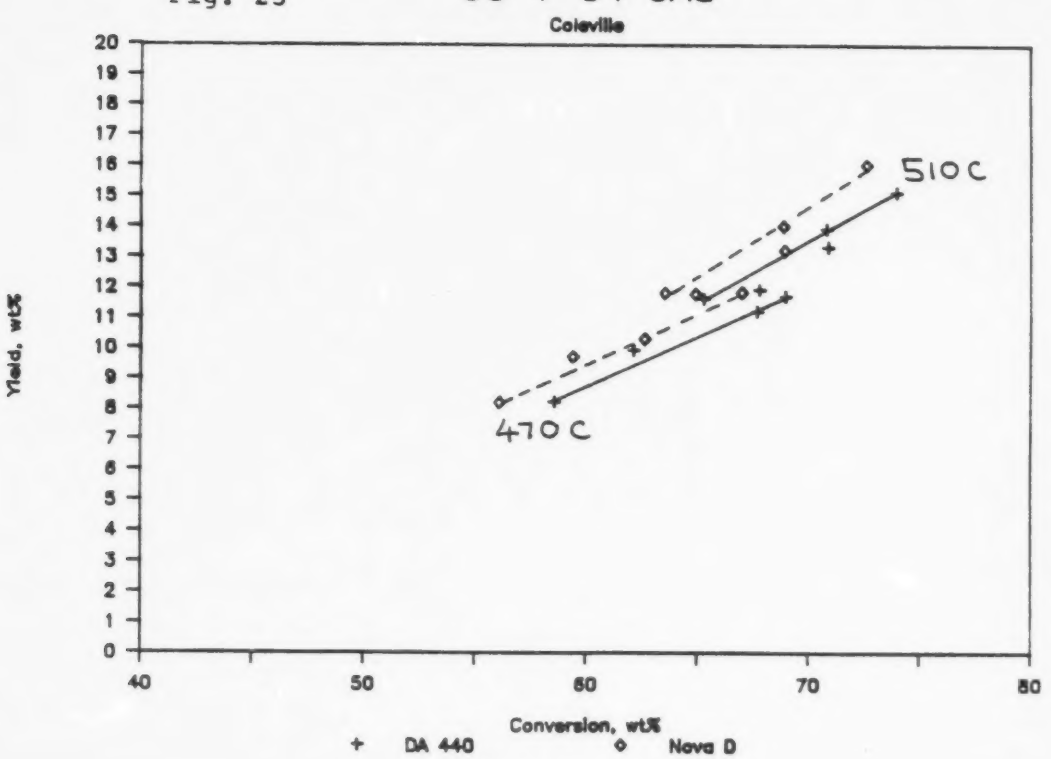

C3 + C4 GAS
Coleville
Yield, wt%
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
40
50
60
70
80
510 C
470 C
Conversion, wt%
+ DA 440
◇ Nova D

Fig. 21

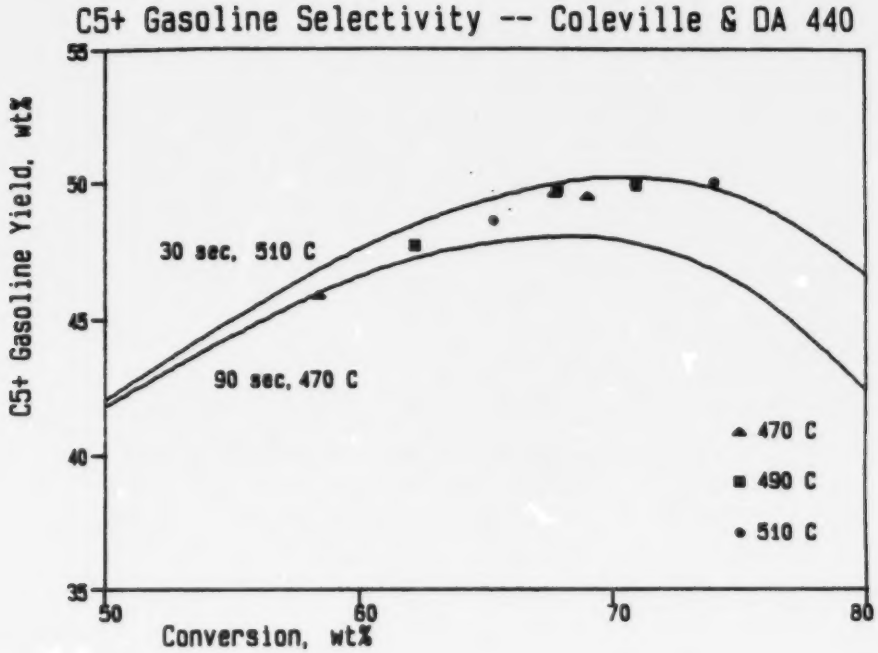

C5+ Gasoline Selectivity -- Coleville & DA 440
C5+ Gasoline Yield, wt%
55
50
45
40
35
30 sec, 510 C
90 sec, 470 C
470 C
490 C
510 C
50
60
70
80
Conversion, wt%

Fig. 22

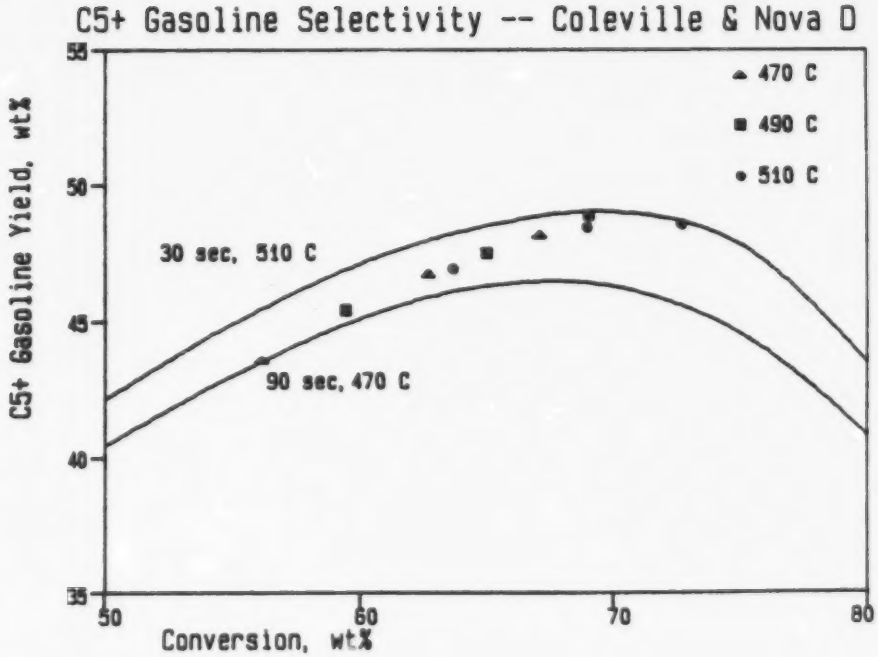
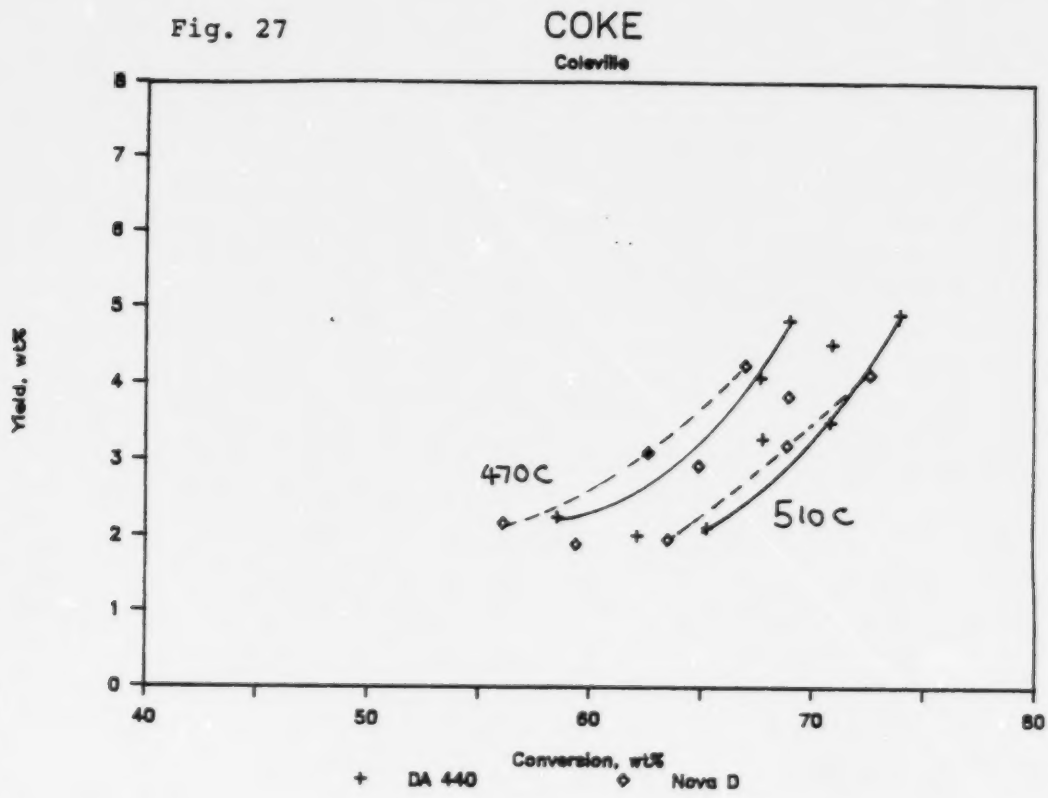

C5+ Gasoline Selectivity -- Coleville & Nova D
C5+ Gasoline Yield, wt%
55
50
45
40
35
470 C
490 C
510 C
30 sec, 510 C
90 sec, 470 C
50
60
70
80
Conversion, wt%

Fig. 27


COKE
Coleville
Yield, wt%
0
1
2
3
4
5
6
7
8
40
50
60
70
80
470C
510C
Conversion, wt%
+ DA 440
◇ Nova D

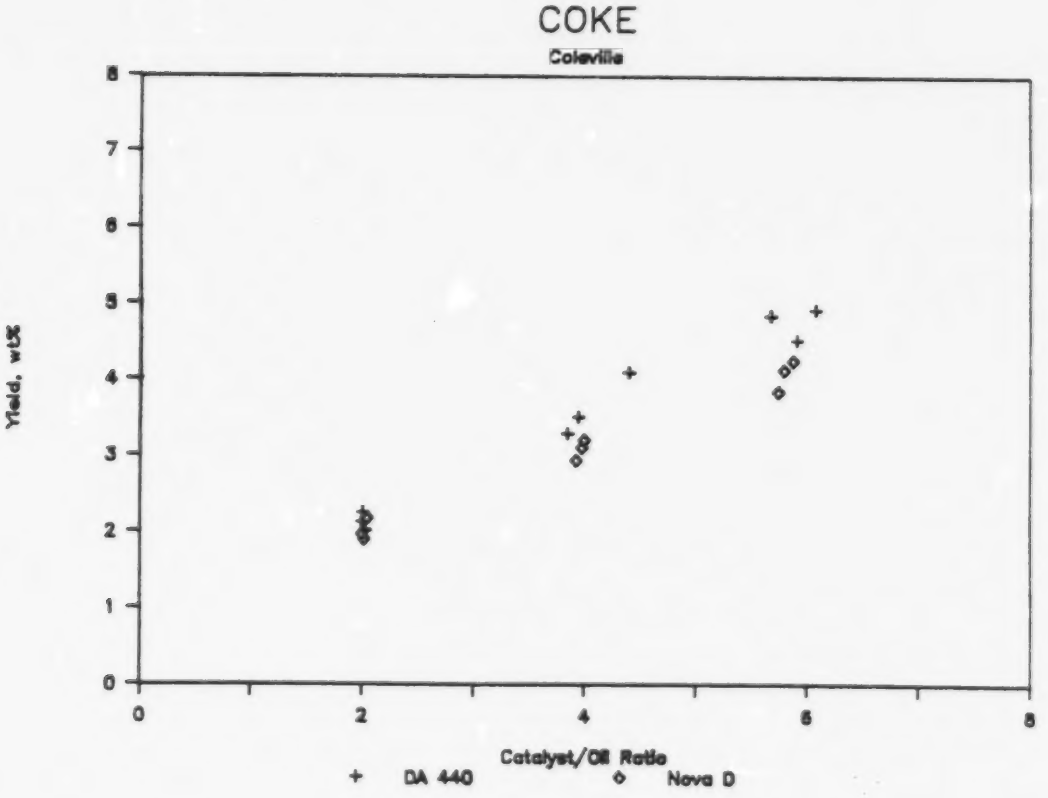

COKE
Coleville
Yield, wt%
0
1
2
3
4
5
6
7
8
0
2
4
6
8
Catalyst/Oil Ratio
+ DA 440
◇ Nova D

Fig. 25

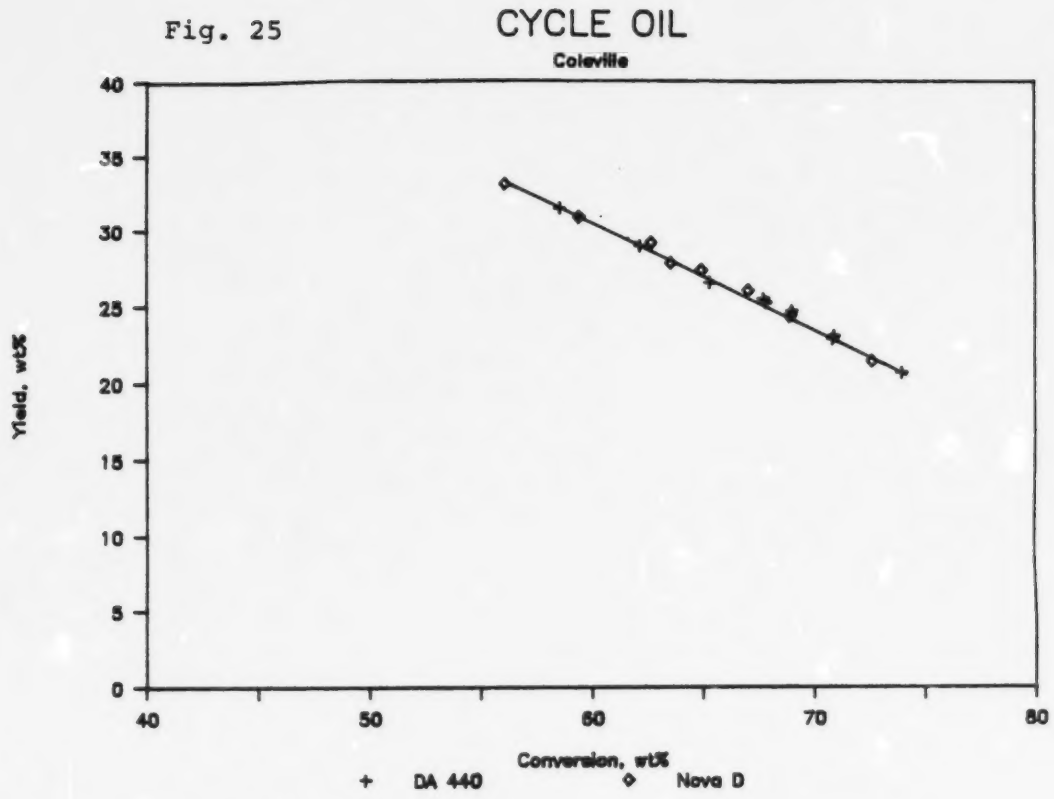
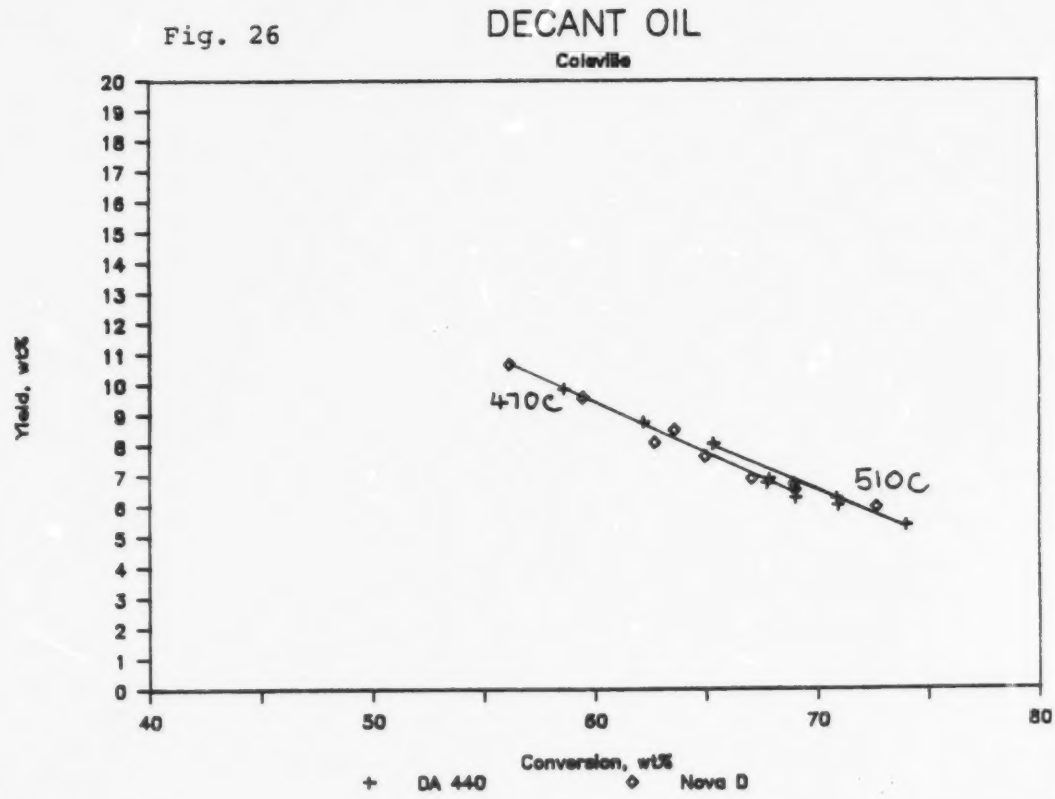

CYCLE OIL
Coleville
Yield, wt%
40
35
30
25
20
15
10
5
0
40
50
60
70
80
Conversion, wt%
+ DA 440
◇ Nova D

Fig. 26


DECANT OIL
Coleville
Yield, wt%
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
40
50
60
70
80
Conversion, wt%
+ DA 440
◇ Nova D
470C
510C

CRACKING CHARACTERISTICS OF LLOYDMINSTER GAS OIL LHOF 16-2

Lloyd is the other non-conventional straight run gas oil i.e. has not received any prior processing. In general, this oil was expected to behave in a similar manner to Coleville gas oil with the proviso that it was a more refractory oil with less gasoline precursors.

Comparison of Coleville and Lloyd Gas Oils

	Wt% Crackable Components	Max. wt% Gasoline	100 wt% refractory components	Max wt% Conversion
Coleville	67.7	50.1	72.5	74.0
Lloyd	60.3	45.6	68.6	69.1

The principal compositional difference between the two feedstocks is a decreased paraffin content of the Lloyd sample (3.75 vs 12.07 wt%) which is compensated by an increased aromatics content.

At the low reactor temperature (470C) both catalysts give approximately equivalent conversion for the Lloyd gas oil for the three different C/O,

		Wt% Conversion		
Nominal C/O		2	4	6
Nova D	470C	51.13	60.40	63.67
DA-440	470C	50.96	59.48	63.71
Nova D	510C	52.72	60.97	66.86
DA-440	510C	54.82	64.70	69.13

while at the higher reactor temperatures, DA-440 is the most active catalyst.

At the highest severity investigated, the conversion achieved using DA-440 just exceeded the compositional conversion constraint (68.6 wt%) while conversion achieved with Nova D was always below this value.

The temperature effect on conversion is shown in Fig.28 & 29 which plots conversion vs C/O for the three reactor temperatures. There is little differentiation between the temperature effects for Nova D except at the high C/O ratio while there is a significant spread for DA-440. The conversion differences between temperatures should be related

to the variations in the cracking rate with temperature.

$$\text{rate of cracking} = Ko\, y^{2}\, e^{-\alpha t}$$

The overall rate constant for cracking Ko and catalyst decay constant for the Coleville and Lloyd gas oils cracking over Nova D catalyst at the three reactor temperatures are compared below.

Comparison of Rate and Decay Constants for Coleville and Lloyd Gas Oil over Nova D Catalyst.

Reactor temp.	470C	490C	510C
Rate Constant ko			
Coleville	45.0	49.5	58.6
Lloyd	41.1	43.2	46.6
Decay Constant			
Coleville	52.7	48.7	47.5
Lloyd	60.2	63.0	65.4

For the Coleville gas oil cracked over Nova D, the decay constant decreases with increasing temperature, thus re-enforcing the positive temperature effect on the rate constant, spreading the conversions vs C/O lines. Whereas, with the Lloyd gas oil, the decay constant increases with temperature, counteracting the positive temperature effect on the rate constant ko, thus contracting the conversion vs C/O lines.

The C5+ gasoline yield vs conversion plots are shown in Figs.30 & 31. Again there is no definite sign of overcracking, although the gasoline make at a C/O of 6 is on average only marginally greater than the gasoline make at a C/O of 4.

Inspection of the C6+ gasoline make (Table 13) shows there may be overcracking with DA-440 at 490C and 510C.

DA-440 / Lloyd C6+ Gasoline Yield

Nominal C/O		2	4	6
Reactor Temp.	490C	36.4	39.77	39.01
	510C	35.66	38.94	38.55

The differences may be within the experimental error of

determining C6+ gasoline.

At a reactor temperature of 470C as discussed earlier, both catalysts give equivalent conversion of the Lloyd gas oil. At this temperature, the selectivity to C5+ gasoline is closely similar for the two catalysts. However, the trend noted earlier of DA-440 favouring C6+ gasoline production while Nova D favours C5 production as well as C3C4 make is also seen here. (See Tables 13 & 14).

At the higher reactor temperature, DA-440 catalyst is more active and more selective for gasoline production i.e. it will produce more gasoline from the Lloyd gas oil than the Nova D catalyst at both constant severity and constant conversion (this agrees with the previous data). The plot of wt% C3C4 yield vs conversion is shown in Fig. 32. At 470C the two catalysts show identical behaviour. At the higher temperature (as noted for the Coleville gas oil) the Nova D catalyst yields more C3C4 than the DA-440 catalyst at constant conversion but both catalysts are equivalent at constant severity.

A similar trend is noted for the dry gas make (Fig.33) and the comments made for the Coleville gas oil apply here. This feed produced a large amount of H2S (2.14 wt% max.) which translates to 7 lb. sulphur/bbl of feed processed.

The Lloyd gas oil contains 25 wt% of 343C minus material and the LCO yield for the 18 MAT runs ranged from a maximum of 33.23 wt% to a minimum of 23.05 wt% (see Tables 13 & 14). A plot of LCO yield vs conversion (Fig.34) shows that there is a minor temperature effect, with at constant conversion, the higher temperature (and lower C/O) producing less LCO and more decant oil. This is again illustrated in Fig.35, the decant oil yield vs conversion plot.

At the lower reactor temperature, there is a minor difference in the LCO/DO ratio for the two catalysts, the Nova D tending to favour LCO production while the DA-440 yields more decant oil at constant conversion.

Also for the Nova D catalyst at constant C/O, the decant oil yield increases marginally with increasing temperature. This may be associated with the relatively poor performance of the Nova D catalyst in cracking Lloyd gas oil at higher temperatures.

The coke selectivity plot Fig.36 shows that there is no difference between the two catalysts when operating at 470C and 510C. At 490C the DA-440 apparently makes less coke at

equivalent conversion.

This feedstock produced more coke per unit of conversion than either the IPL, Coleville or Suncor gas oil.

Fig. 28

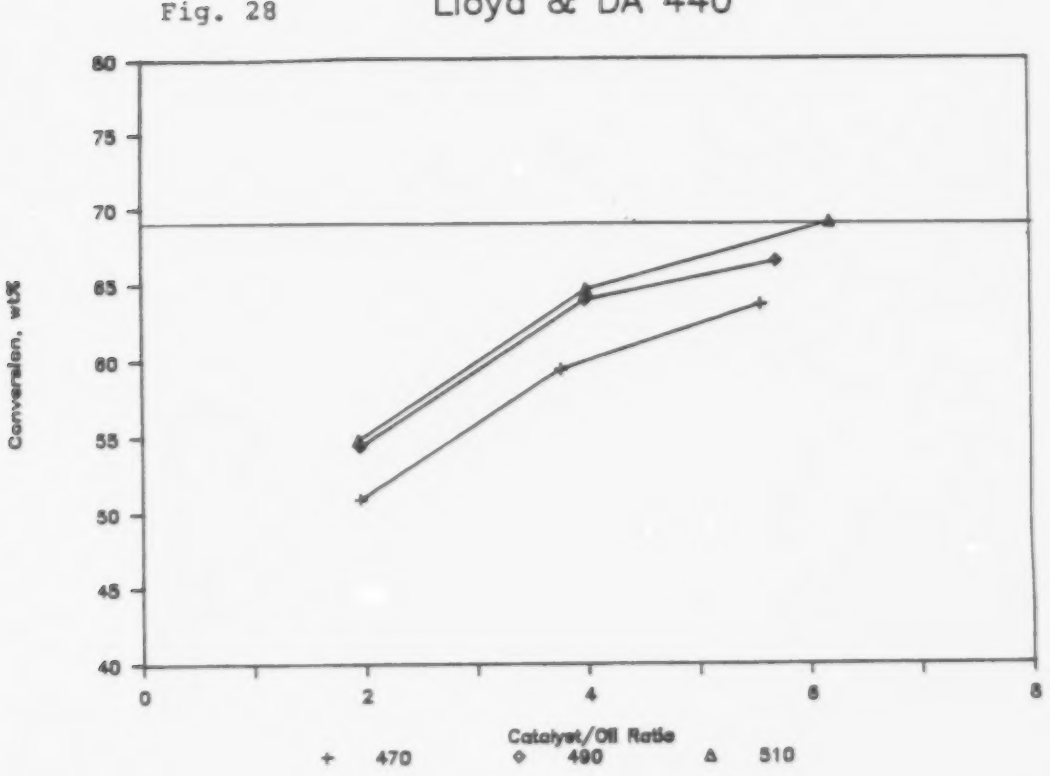

Lloyd & DA 440
80
75
70
65
60
55
50
45
40
Conversion, wt%
0
2
4
6
8
Catalyst/Oil Ratio
+ 470
◇ 490
△ 510

Fig. 29

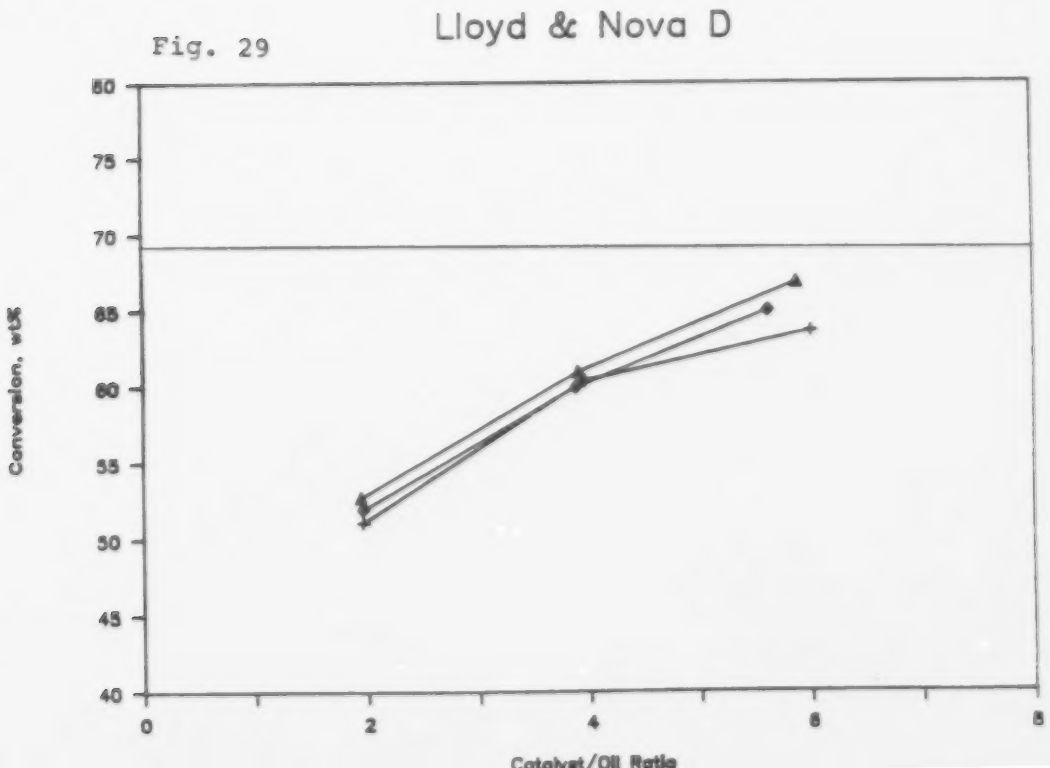

Lloyd & Nova D
80
75
70
65
60
55
50
45
40
Conversion, wt%
0
2
4
6
8
Catalyst/Oil Ratio

Table 13

MICROACTIVITY TEST RESULTS USING
DA-440 EQUILIBRIUM CATALYST AND
LLOYD GAS OIL

RUN NO.	84	86	88	78	80	82	72	74	76
Reactor TempC	470	470	470	490	490	490	510	510	510
WHSV HR-1	20.00	20.50	21.00	19.80	19.60	20.40	20.00	19.50	19.00
C/O	1.96	3.77	5.57	1.96	3.99	5.71	1.94	4.00	6.20
H2	0.01	0.02	0.02	0.02	0.02	0.03	0.02	0.03	0.04
H2S	1.69	1.99	2.00	1.79	2.04	2.13	1.74	1.98	2.05
C1	0.12	0.17	0.22	0.20	0.30	0.38	0.31	0.45	0.59
C2	0.17	0.23	0.29	0.24	0.36	0.42	0.33	0.47	0.57
C2-	0.25	0.38	0.46	0.34	0.52	0.63	0.42	0.63	0.79
Total Dry Gas	2.24	2.79	2.99	2.59	3.24	3.59	2.82	3.56	4.04
C3	0.48	0.77	1.04	0.60	1.02	1.26	0.72	1.13	1.52
C3-	1.78	2.25	2.41	2.19	2.78	2.93	2.41	3.06	3.29
i-C4	2.33	3.29	3.77	2.66	3.77	4.27	2.72	3.76	4.48
n-C4	0.43	0.68	0.84	0.52	0.85	1.04	0.59	0.91	1.17
C4-	1.74	2.09	2.17	2.09	2.47	2.56	2.30	2.79	2.73
Total C3C4	6.76	9.08	10.23	8.06	10.89	12.06	8.74	11.65	13.19
i-C5	2.37	3.45	3.95	2.71	3.94	4.48	2.78	3.91	4.78
n-C5	0.30	0.30	0.33	0.37	0.37	0.47	0.41	0.44	0.47
C5-	1.45	1.20	1.31	1.71	1.54	1.43	1.76	1.67	1.54
Total C5	4.12	4.95	5.59	4.79	5.85	6.38	4.95	6.02	6.79
C5-216C	39.34	43.34	44.84	41.19	45.62	45.39	40.61	44.96	45.34
C6-216C	35.22	38.39	39.25	36.40	39.77	39.01	35.66	38.94	38.55
216-343C	32.92	29.40	27.16	30.96	26.54	25.08	29.46	25.62	23.05
343C-E.P.	16.12	11.12	9.13	14.64	9.46	8.36	15.72	9.68	7.82
Coke	2.63	4.27	5.63	2.55	4.25	5.53	2.65	4.54	6.55
Conversion	50.96	59.48	63.71	54.40	64.00	66.55	54.82	64.70	69.13
Material Balance	99.62	99.20	100.29	99.38	99.24	99.30	99.74	99.38	100.82

Table 14

MICROACTIVITY TEST RESULTS USING
NOVA D EQUILIBRIUM CATALYST AND
LLOYD GAS OIL

RUN NO.	83	85	89	77	79	81	71	73	75
Reactor TempC	470	470	470	490	490	490	510	510	510
WHSV HR-1	19.70	19.70	20.00	19.60	19.80	20.30	19.80	20.00	20.00
C/O	1.97	3.97	6.01	1.97	3.89	5.62	1.95	3.91	5.88
H2	0.02	0.03	0.05	0.03	0.04	0.05	0.04	0.05	0.07
H2S	1.80	1.99	2.08	1.80	1.83	2.09	1.76	1.96	2.14
C1	0.14	0.20	0.23	0.22	0.29	0.38	0.32	0.47	0.61
C2	0.18	0.26	0.30	0.25	0.32	0.39	0.32	0.45	0.56
C2-	0.24	0.37	0.45	0.31	0.44	0.57	0.38	0.57	0.74
Total Dry Gas	2.38	2.85	3.11	2.61	2.92	3.48	2.82	3.50	4.12
C3	0.44	0.74	0.96	0.56	0.82	1.09	0.63	1.00	1.36
C3-	1.86	2.34	2.54	2.14	2.46	2.88	2.41	2.96	3.45
i-C4	2.39	3.32	3.94	2.47	3.21	4.04	2.49	3.51	4.39
n-C4	0.40	0.63	0.80	0.47	0.66	0.86	0.53	0.76	1.04
C4-	1.88	2.28	2.38	2.21	2.35	2.70	2.55	2.83	3.13
Total C3C4	6.97	9.31	10.62	7.85	9.50	11.57	8.61	11.06	13.37
i-C5	2.39	3.49	4.13	2.46	3.36	4.19	2.48	3.46	4.44
n-C5	0.35	0.33	0.34	0.36	0.35	0.34	0.47	0.41	0.43
C5-	1.65	1.40	1.33	1.83	1.51	1.52	1.94	1.95	1.61
Total C5	4.39	5.22	5.80	4.65	5.22	6.05	4.89	5.82	6.48
C5-216C	39.04	43.92	44.45	38.98	43.62	44.57	38.76	42.16	43.86
C6-216C	34.65	38.70	38.65	34.33	38.40	38.52	33.87	36.34	37.38
216-343C	33.23	29.18	27.43	31.93	28.95	26.04	30.64	27.53	24.47
343C-E.P.	15.63	10.41	8.90	16.13	11.07	8.97	16.64	11.50	8.67
Coke	2.73	4.32	5.49	2.47	3.94	5.38	2.54	4.25	5.50
Conversion	51.13	60.40	63.67	51.94	59.97	64.99	52.72	60.97	66.86
Material Balance	99.45	100.04	100.40	99.11	101.55	100.77	99.28	100.64	99.61

Fig. 30

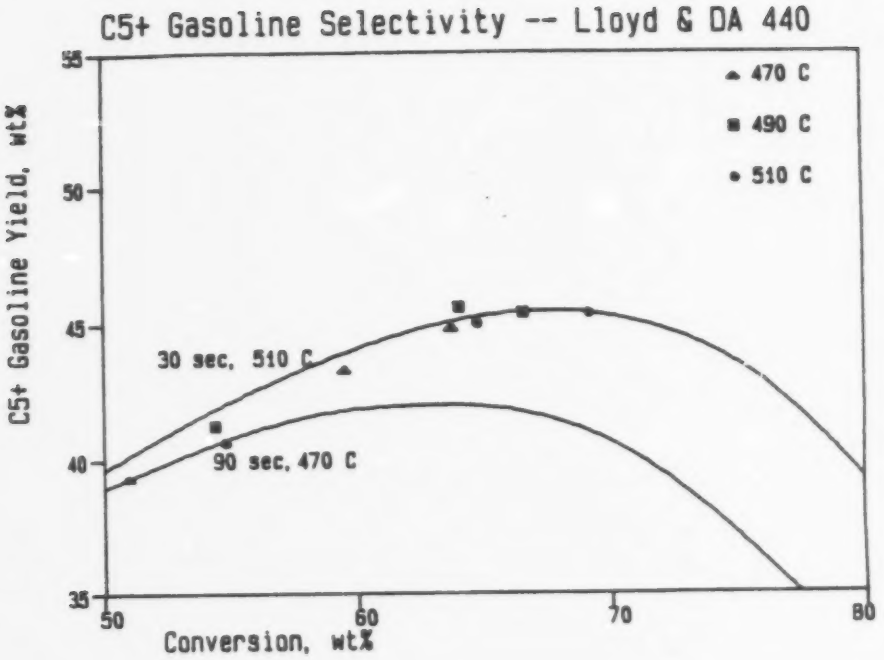

C5+ Gasoline Selectivity -- Lloyd & DA 440
C5+ Gasoline Yield, wt%
Conversion, wt%
470 C
490 C
510 C
30 sec, 510 C
90 sec, 470 C
55
50
45
40
35
50
60
70
80

Fig. 31

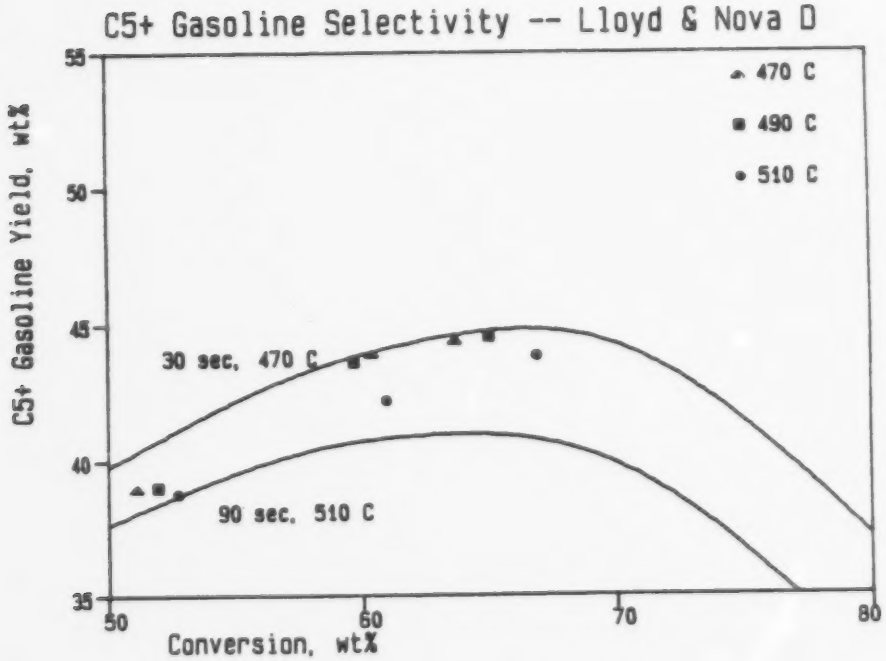

C5+ Gasoline Selectivity -- Lloyd & Nova D
C5+ Gasoline Yield, wt%
Conversion, wt%
470 C
490 C
510 C
30 sec, 470 C
90 sec, 510 C
55
50
45
40
35
50
60
70
80

Fig. 33

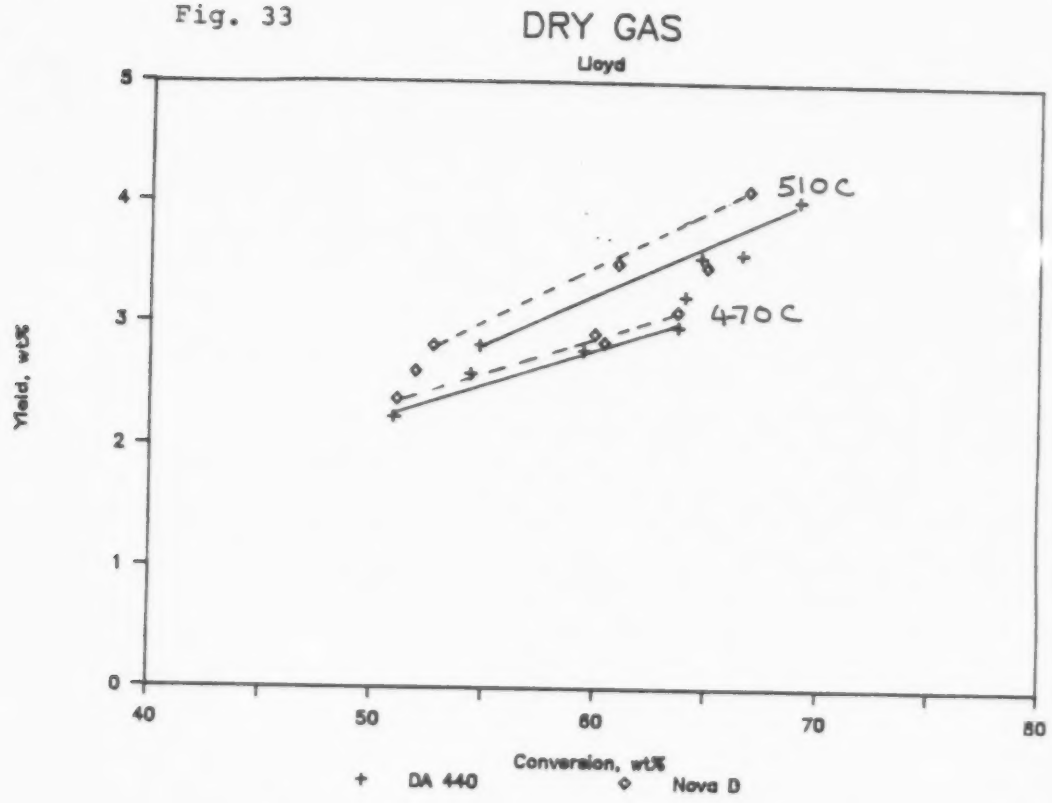

DRY GAS
Lloyd
510C
470C
Yield, wt%
Conversion, wt%
DA 440
Nova D

Fig. 32

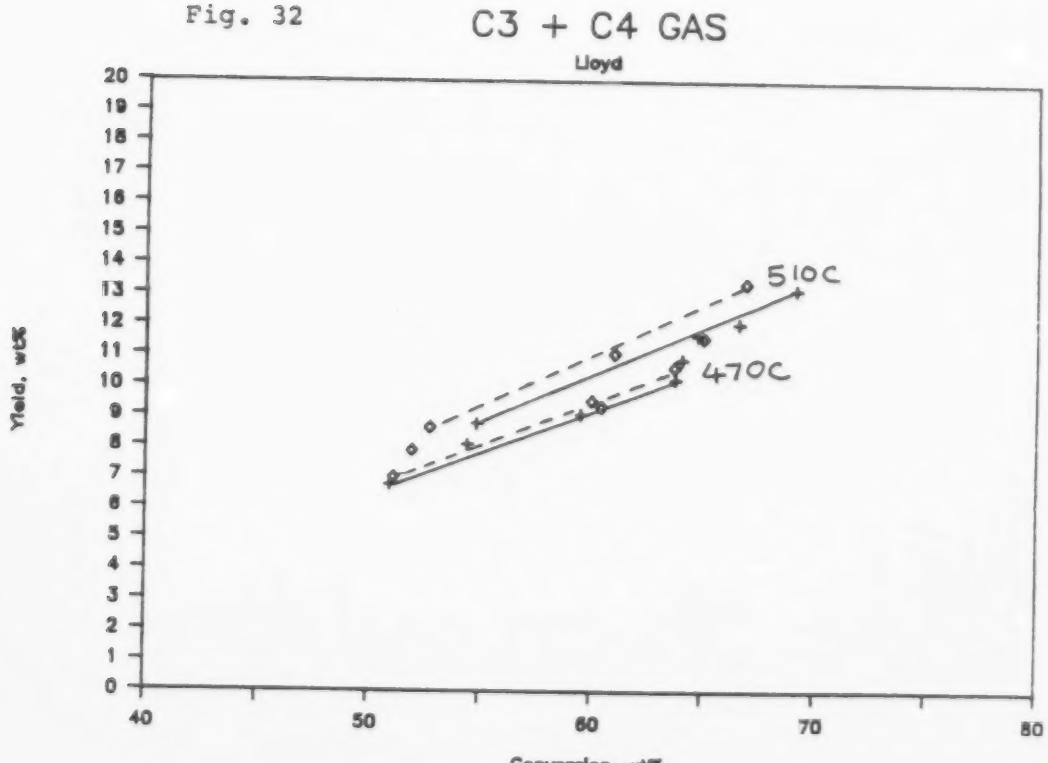

C3 + C4 GAS
Lloyd
510C
470C
Yield, wt%

Fig. 34

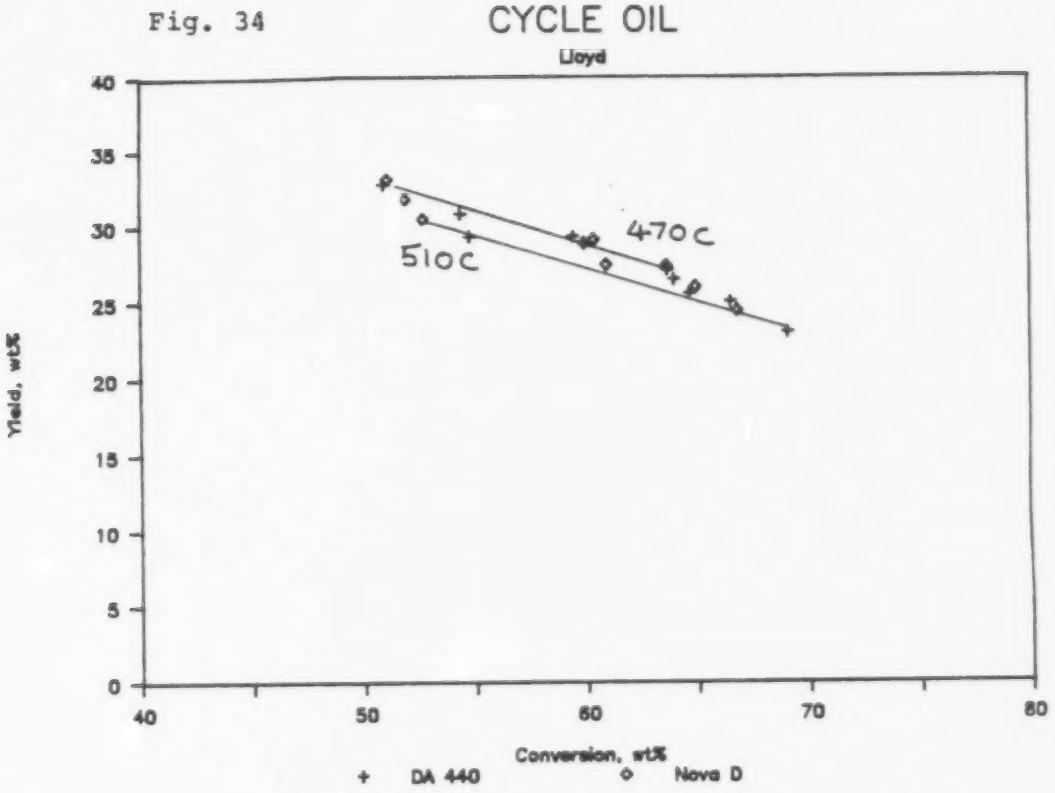

CYCLE OIL
Lloyd
470C
510C
Yield, wt%
Conversion, wt%
+ DA 440
◇ Nova D

Fig. 35

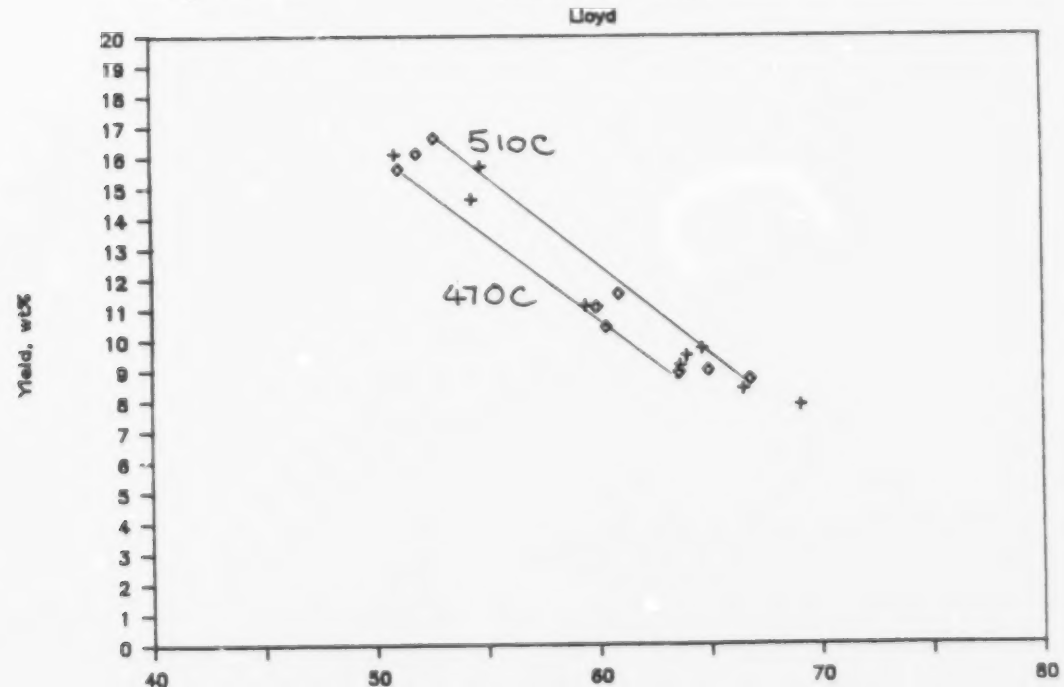
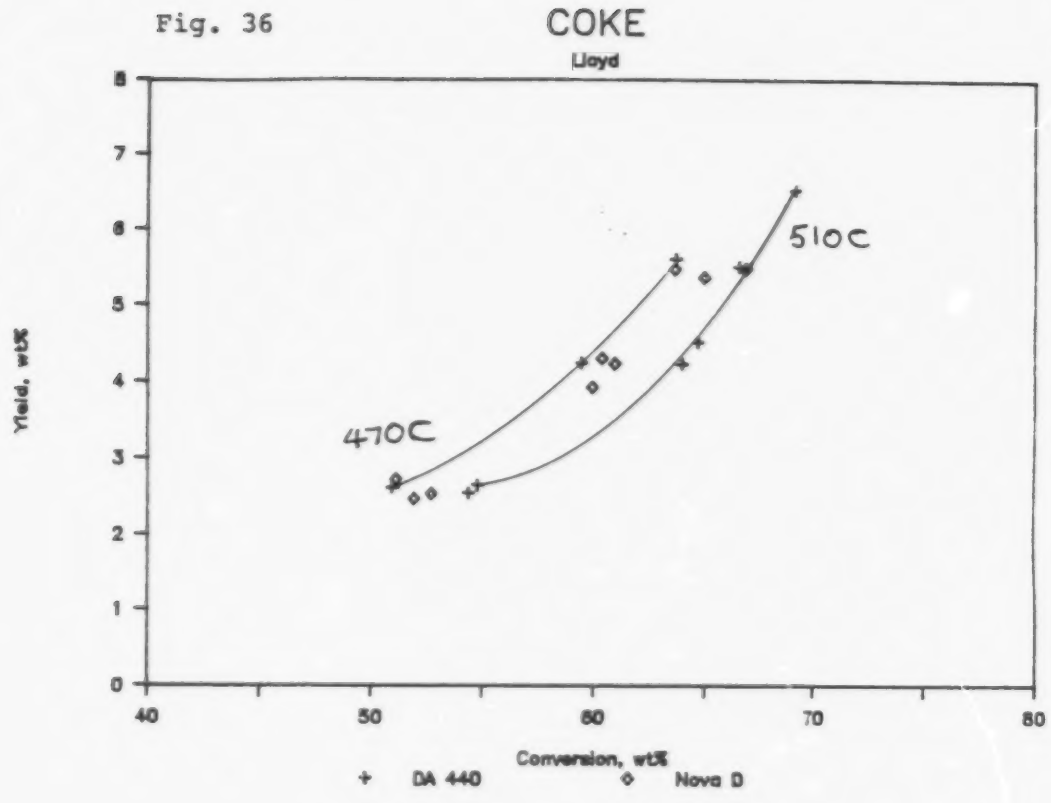
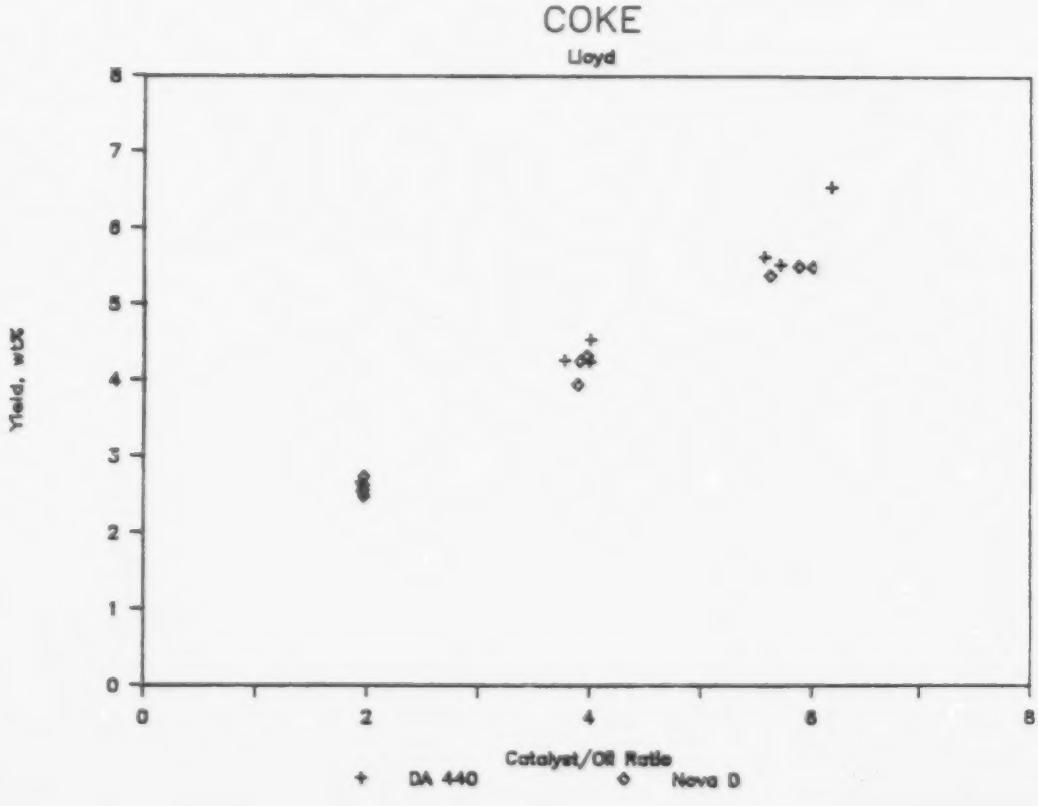

DECANT OIL
Lloyd
510C
470C
Yield, wt%

Fig. 36


COKE
Lloyd
Yield, wt%
Conversion, wt%
470C
510C
DA 440
Nova D


COKE
Lloyd
Yield, wt%
Catalyst/Oil Ratio
DA 440
Nova D

CRACKING CHARACTERISTICS OF SUNCOR GAS OIL SF-164

SF-164 was the first of the processed gas oils studied. Processing at the Suncor Plant (GCOS) essentially involves thermally cracking Athabasca bitumen in a delayed coker followed by distillation and hydrotreating of the various product streams.

The conversion vs C/O ratio plots for Suncor gas oil are shown in Figs. 37 & 38 and the yield data is presented in Tables 15 & 16. Maximum conversion achieved (using DA-440, C/O of 5.8 and reactor temperature 510C) was lower than the calculated compositional conversion constraint.

Maximum Conversion	69.1 wt%
(100-wt%) Refractory Components	73.7 wt%

This suggests that this processed stock requires higher severity or more active catalyst to achieve optimum conversion.

This is also shown by comparing the overall rate constant for cracking ko with that calculated for the Coleville and Lloyd gas oils.

Gas Oil Rate Constants with DA-440 Catalyst

Reactor Temp.	470	490	510
Suncor	40.1	47.7	49.9
Lloyd	46.7	51.6	53.7
Coleville	54.7	59.6	64.2

As can be seen, the Suncor gas oil has the lower rate constant and is more difficult to crack.

The variation of conversion with C/O ratio and reactor temperature (Figs.37 & 38) are regular as would be expected. The conversion shows that the DA-440 catalyst is more active for cracking Suncor gas oil than the Nova D catalyst. This is also reflected in the average higher rate constant for cracking obtained when using the DA-440 catalyst. (See Tables 7 & 8).

The C5+ gasoline yield vs conversion plots are shown in Figs.39 & 40. Again there is no definite sign of overcracking although the gasoline yield increase is only marginal when increasing the C/O from 4 to 6. Inspection of the C6+ gasoline make (Tables 15 & 16)) shows minimal signs of overcracking.

When comparing C5+ gasoline yields at constant severity, the DA-440 catalyst will yield only marginally more gasoline than the Nova D catalyst (0.5 wt% on average). Comparing the two catalysts at constant conversion (Figs.39 & 40) shows even less differentiation. The performance of the two catalysts are equivalent at low conversion and the DA-440 is marginally more selective at higher conversions. The difference generally is close to an experimental error in the gasoline yield.

When comparing the selectivity for C5+ gasoline production at equivalent conversion for the three non-conventional gas oils, it is found that when DA-440 is used as the catalyst, the order is Coleville > Suncor > Lloyd. When the Nova D is used as a catalyst, the Coleville and Suncor sample give equivalent selectivity and are both significantly better than the Lloyd samples.

The C3C4 yield vs conversion plots (Fig.41) show that this processed gas oil behaved somewhat differently from the straight run gas oils. At the lower reactor temperature (470C), there is little differentiation between the two catalysts in terms of C3C4 yield vs conversion. At 510C and equal conversion, the DA-440 catalyst produces marginally more C3C4 components. This is the reverse of what was found for the three straight run feedstocks and what would be expected based on hydrogen transfer, where the octane enhancing catalyst may produce light liquids at the expense of gasoline range components. It must be assumed that the gasoline produced by cracking Suncor gas oil with Nova D is relatively deficient in olefins and thus there is little opportunity for the Nova D catalyst to overcrack these components to light liquids.

The trend in dry gas make with conversion is as would be expected (see Fig.42). For constant conversion, the dry gas make increases with temperature and there is litle differentiation between the two catalysts. As already noted, the Nova D catalyst produces more hydrogen. The Suncor gas oil, being hydrotreated, produces only trace amounts of H2S when catalytically cracked (approximately 0.1 lbs/bbl processed).

The Suncor gas oil contained 20 wt% 343C minus material and the LCO yield for the 18 MAT runs ranged from 30.69 weight percent to 22.09 wt%. Thus, there was a net make of distillate material under all cracking conditions. The plot of LCO yield vs conversion (Fig.43) shows that there is a slight temperature effect in that at constant conversion, a decrease in temperature (increase in C/O) would increase the

Table 15

MICROACTIVITY TEST RESULTS USING
DA-440 EQUILIBRIUM CATALYST AND
SUNCOR GAS OIL

RUN NO.	48	49	51	42	45	46	37	35	39
Reactor TempC	470	470	470	490	490	490	510	510	510
WHSV HR-1	19.50	19.60	17.90	19.50	20.60	18.90	19.90	19.80	20.00
C/O	2.02	4.00	6.49	2.05	3.80	6.26	1.95	4.04	5.81
H2	0.02	0.04	0.06	0.02	0.08	0.06	0.04	0.04	0.05
H2S	0.04	0.03	0.03	0.04	0.03	0.04	0.04	0.03	0.03
C1	0.12	0.16	0.21	0.17	0.20	0.41	0.35	0.41	0.52
C2	0.20	0.24	0.27	0.23	0.31	0.37	0.41	0.44	0.55
C2-	0.30	0.38	0.50	0.34	0.47	0.60	0.55	0.63	0.79
Total Dry Gas	0.68	0.85	1.07	0.80	1.09	1.48	1.39	1.55	1.94
C3	0.62	0.88	1.22	0.67	1.02	1.36	1.04	1.26	1.63
C3-	2.01	2.19	2.44	2.16	2.55	2.83	3.22	3.01	3.34
i-C4	2.81	3.39	4.12	2.86	3.57	4.31	3.80	3.90	4.67
n-C4	0.59	0.79	1.11	0.63	0.91	1.21	0.86	1.04	1.34
C4-	1.65	1.98	2.11	2.05	2.33	2.47	2.86	2.65	2.77
Total C3C4	7.68	9.23	11.00	8.37	10.38	12.18	11.78	11.86	13.75
i-C5	2.90	3.61	4.50	3.26	3.91	4.76	3.65	4.03	4.94
n-C5	0.31	0.32	0.36	0.41	0.42	0.41	0.47	0.48	0.51
C5-	1.24	1.12	1.00	1.68	1.72	1.19	1.89	1.61	1.56
Total C5	4.45	5.05	5.86	5.35	6.05	6.36	6.01	6.12	7.01
C5-216C	42.89	45.92	47.64	44.49	47.40	47.59	44.37	47.43	47.82
C6-216C	38.44	40.87	41.78	39.14	41.35	41.23	38.36	41.31	40.81
216-343C	30.63	27.75	24.92	28.81	25.91	23.94	26.02	24.27	22.09
343C-E.P.	15.62	12.24	9.66	15.09	11.33	9.11	14.17	10.75	8.78
Coke	2.51	4.00	5.71	2.44	3.89	5.72	2.27	4.13	5.62
Conversion	53.75	60.01	65.42	56.11	62.76	66.95	59.82	64.98	69.12
Material Balance	99.43	99.77	99.08	100.04	99.12	99.76	97.04	100.00	100.51

Table 16

MICROACTIVITY TEST RESULTS USING
NOVA D EQUILIBRIUM CATALYST AND
SUNCOR GAS OIL

RUN NO.	47	50	52	41	43	44	38	36	40
Reactor TempC	470	470	470	490	490	490	510	510	510
WHSV HR-1	17.60	19.70	19.20	19.20	19.40	19.80	19.40	19.40	20.40
C/O	2.24	3.94	5.85	2.06	4.13	5.94	2.03	4.12	5.87
H2	0.04	0.06	0.04	0.04	0.04	0.09	0.06	0.05	0.08
H2S	0.04	0.04	0.02	0.04	0.03	0.04	0.03	0.03	0.03
C1	0.12	0.15	0.21	0.18	0.23	0.33	0.27	0.47	0.46
C2	0.18	0.23	0.29	0.22	0.28	0.37	0.30	0.42	0.45
C2-	0.26	0.34	0.45	0.31	0.44	0.57	0.39	0.59	0.67
Total Dry Gas	0.64	0.82	1.01	0.79	1.02	1.40	1.05	1.56	1.69
C3	0.54	0.76	1.06	0.57	0.90	1.18	0.67	1.12	1.28
C3-	1.99	2.21	2.56	2.19	2.66	2.93	2.64	3.06	3.20
i-C4	2.66	3.33	4.11	2.80	3.64	4.27	2.99	3.90	4.25
n-C4	0.53	0.67	0.95	0.51	0.78	1.01	0.60	0.94	1.08
C4-	1.96	2.04	2.35	2.07	2.51	2.67	2.65	2.81	2.83
Total C3C4	7.68	9.01	11.03	8.14	10.49	12.06	9.55	11.83	12.64
i-C5	2.74	3.48	4.52	3.20	3.75	4.59	2.99	3.97	5.04
n-C5	0.36	0.34	0.34	0.38	0.39	0.45	0.49	0.47	0.45
C5-	1.38	1.22	1.08	1.75	1.63	1.44	2.09	1.76	1.71
Total C5	4.48	5.04	5.94	5.33	5.77	6.48	5.57	6.20	7.20
C5-216C	43.00	45.24	46.98	43.51	46.28	46.93	44.47	46.49	47.80
C6-216C	38.52	40.20	41.04	38.18	40.51	40.45	38.90	40.29	40.60
216-343C	30.69	28.40	25.86	29.39	26.72	24.70	27.94	24.93	23.20
343C-E.P.	15.43	12.92	10.30	15.85	11.74	10.01	14.85	11.35	9.72
Coke	2.53	3.59	4.82	2.31	3.72	4.90	2.15	3.85	4.97
Conversion	53.88	58.68	63.84	54.77	61.54	65.29	57.21	63.72	67.08
Material Balance	99.85	101.87	100.33	99.66	99.86	99.76	99.59	98.90	101.29

LCO yield at the expense of the decant oil. This can be seen better on the plot of decant oil yield vs conversion (Fig.44). There is no apparent difference in the LCO/DO ratio for the two catalysts.

The coke selectivity plot for the two catalysts is shown in Fig.45. Lines have been drawn through the DA-440 data at 470C and 510C and a dotted line through the equivalent Nova D data. Again the coke selectivity of the two catalysts is closely similar.

Fig. 37 Suncor & DA 440

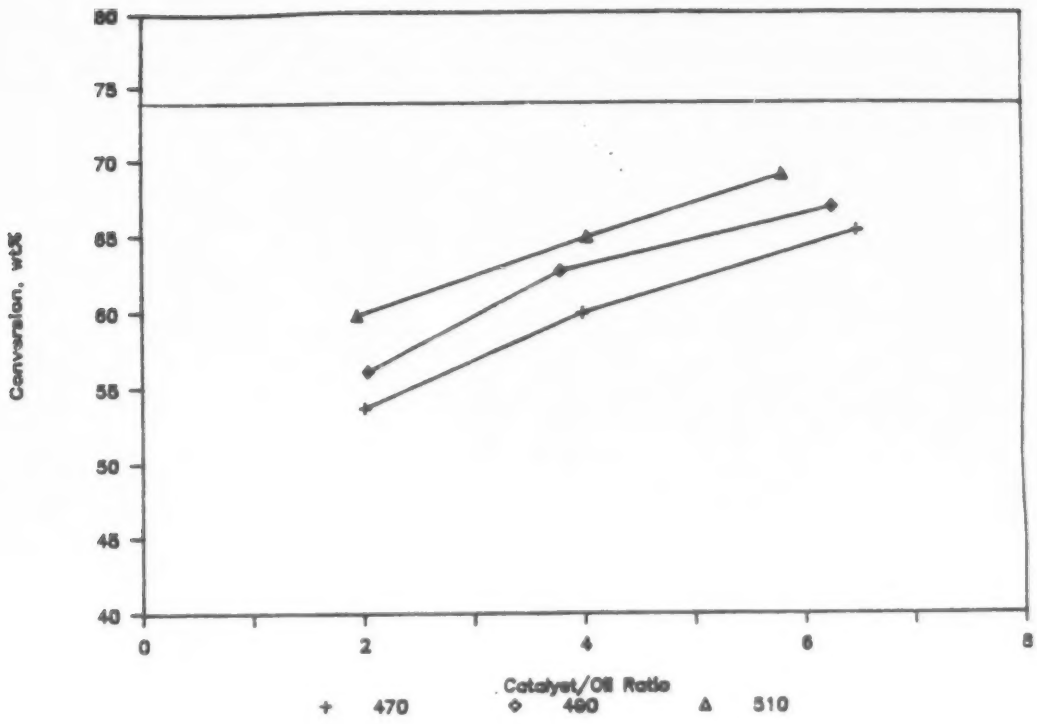


Fig. 38 Suncor & Nova D

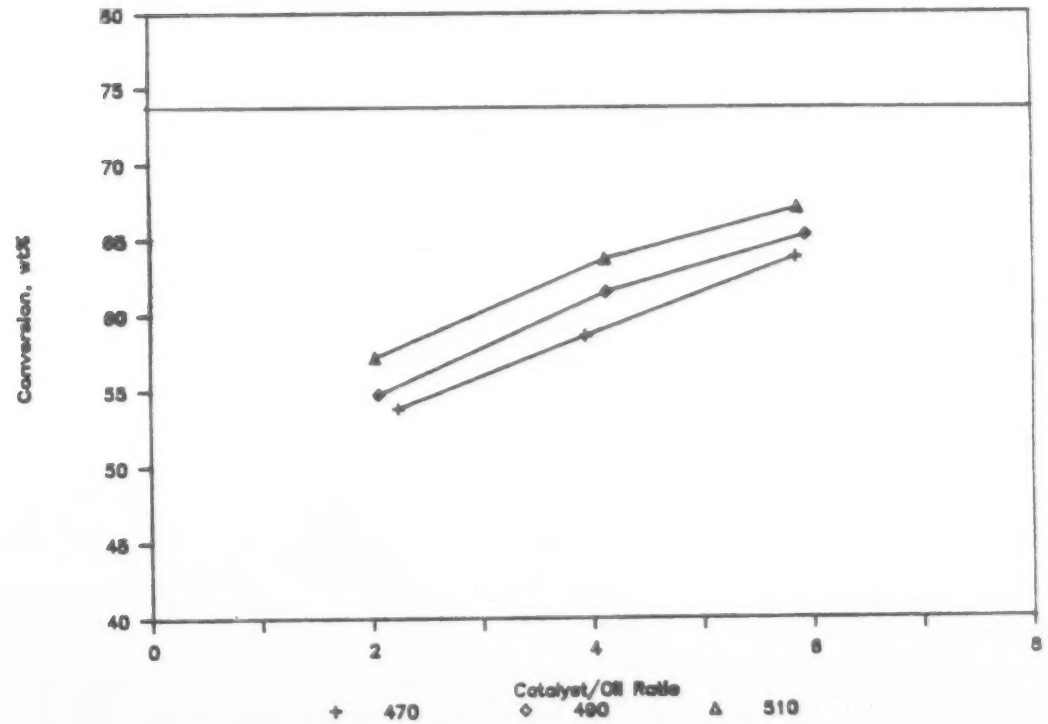


Fig. 39

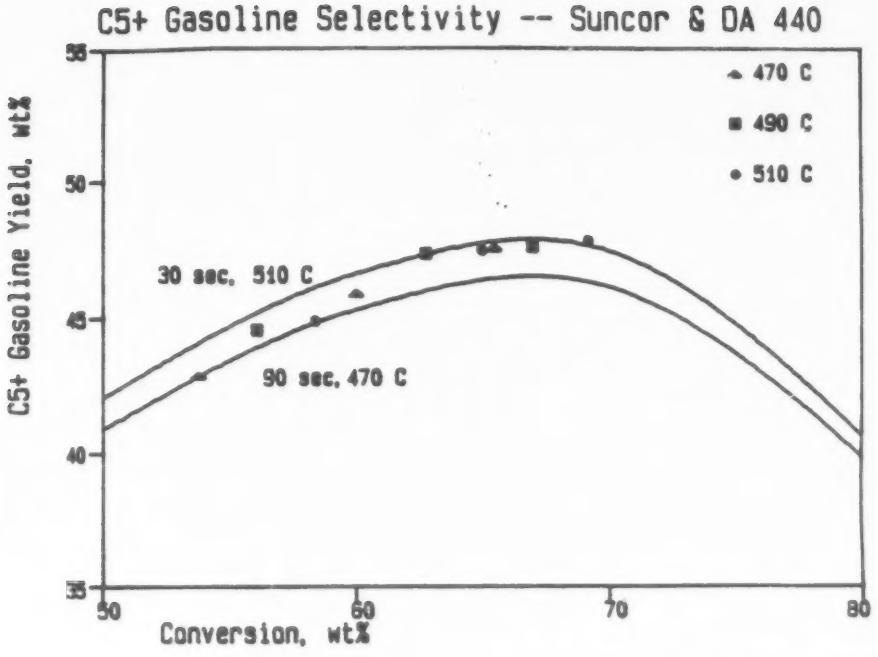

C5+ Gasoline Selectivity -- Suncor & DA 440
C5+ Gasoline Yield, wt%
Conversion, wt%
470 C
490 C
510 C
30 sec, 510 C
90 sec, 470 C
55
50
45
40
35
50
60
70
80

Fig. 40

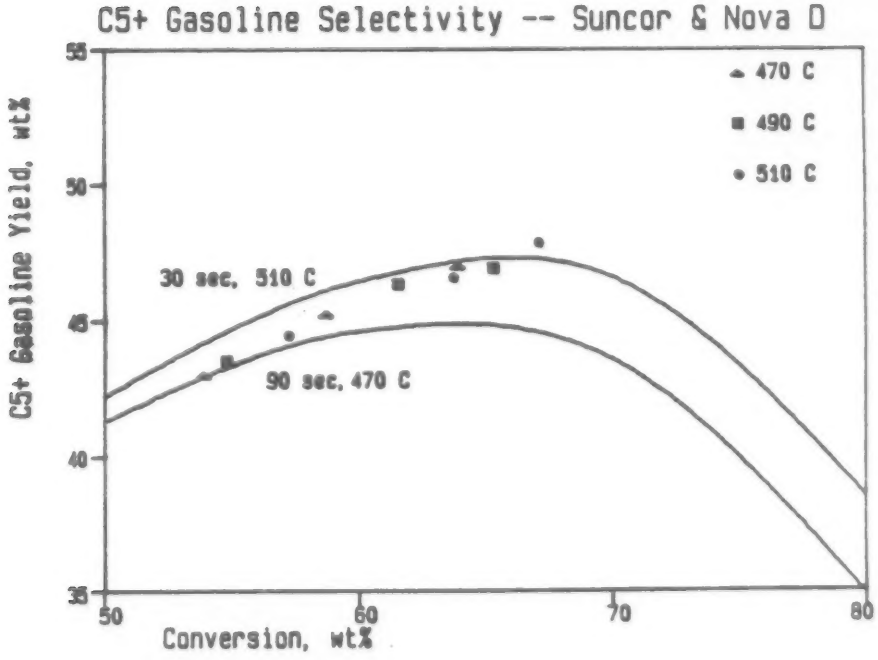

C5+ Gasoline Selectivity -- Suncor & Nova D
C5+ Gasoline Yield, wt%
Conversion, wt%
470 C
490 C
510 C
30 sec, 510 C
90 sec, 470 C
55
50
45
40
35
50
60
70
80

Fig. 42

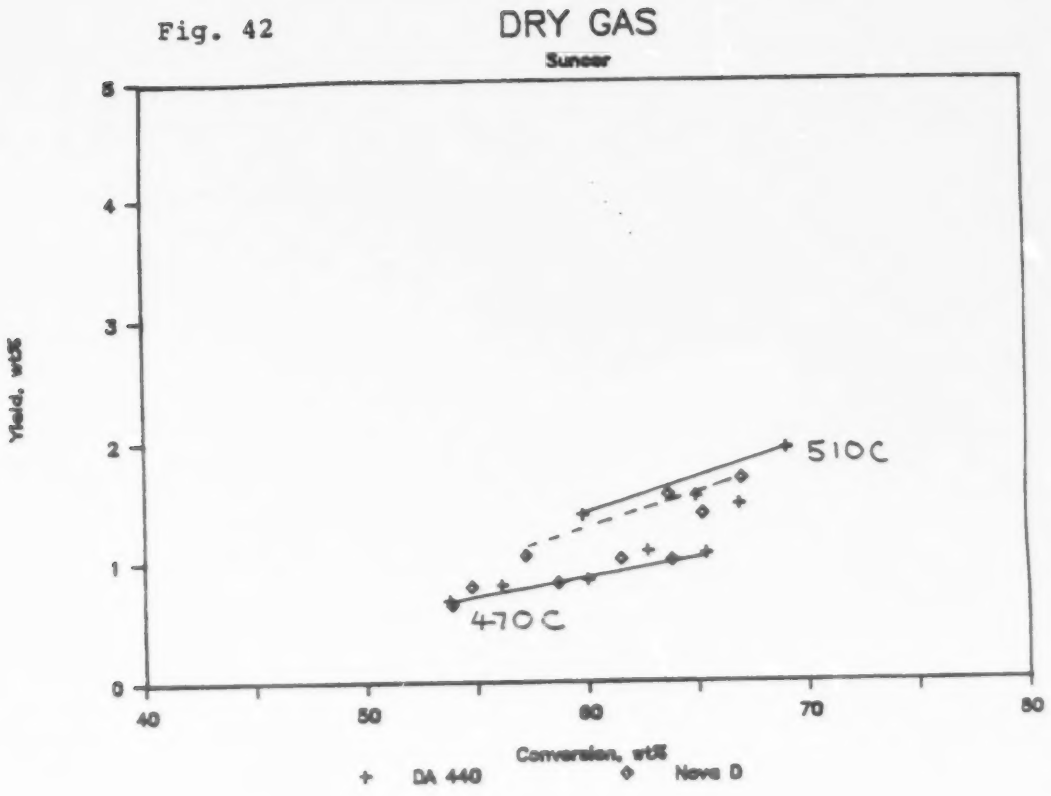

DRY GAS
Sunoar
Yield, wt%
0
1
2
3
4
5
40
50
60
70
80
510C
470C
Conversion, wt%
DA 440
Nova D

Fig. 41

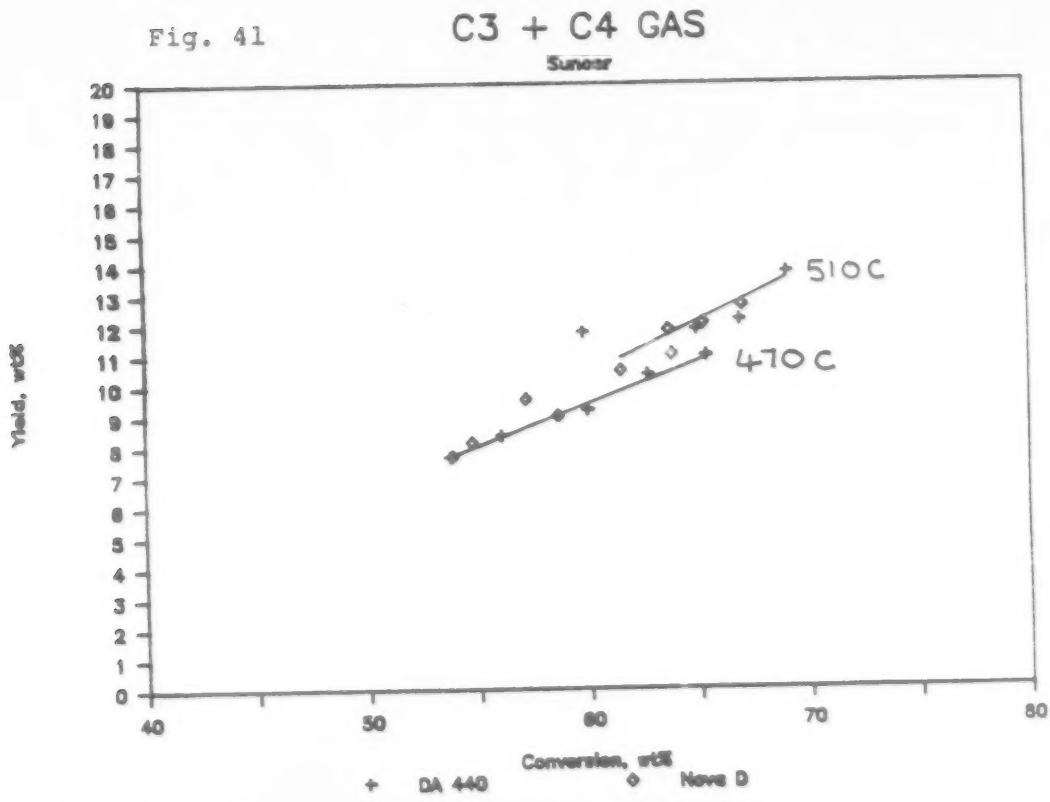

C3 + C4 GAS
Sunoar
Yield, wt%
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
40
50
60
70
80
510C
470C
Conversion, wt%
DA 440
Nova D

Fig. 43

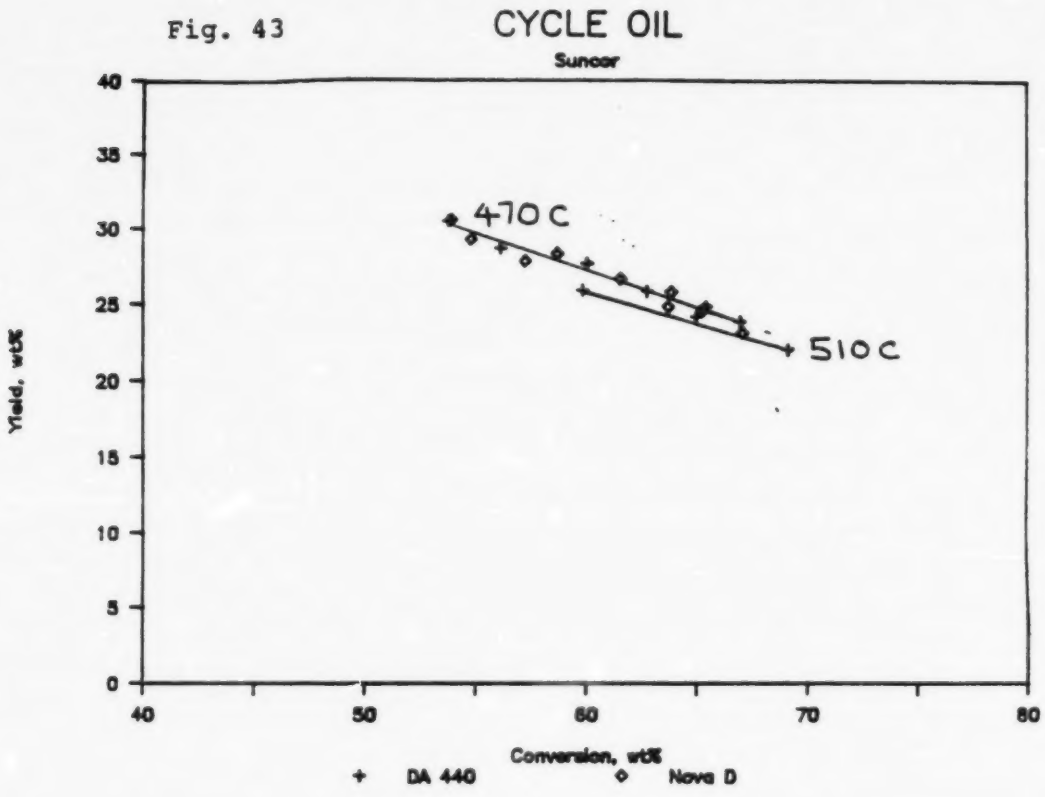

CYCLE OIL
Suncor
470 C
510 C
Yield, wt%
Conversion, wt%
DA 440
Nova D

Fig. 44

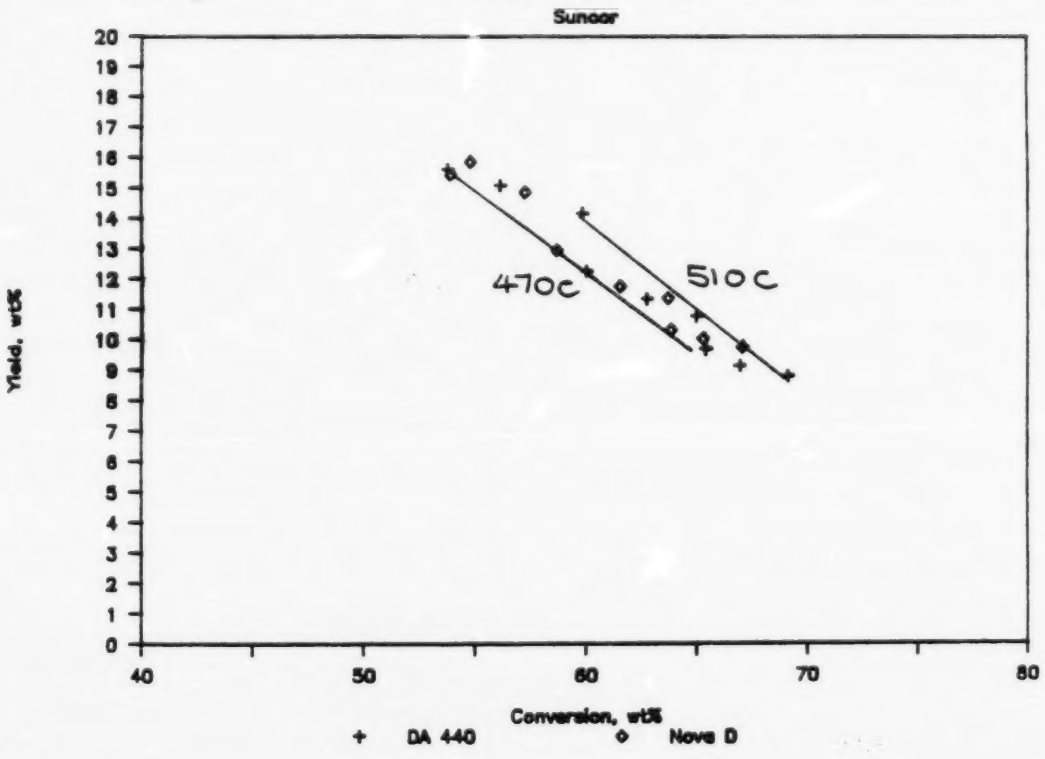
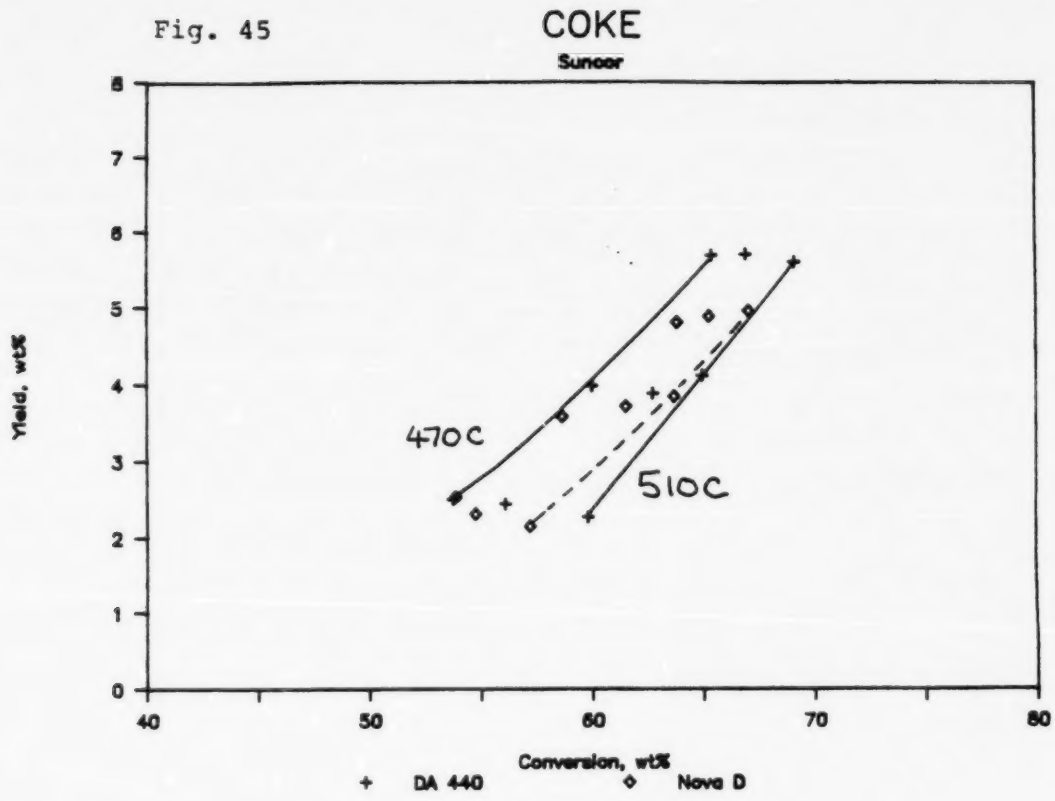
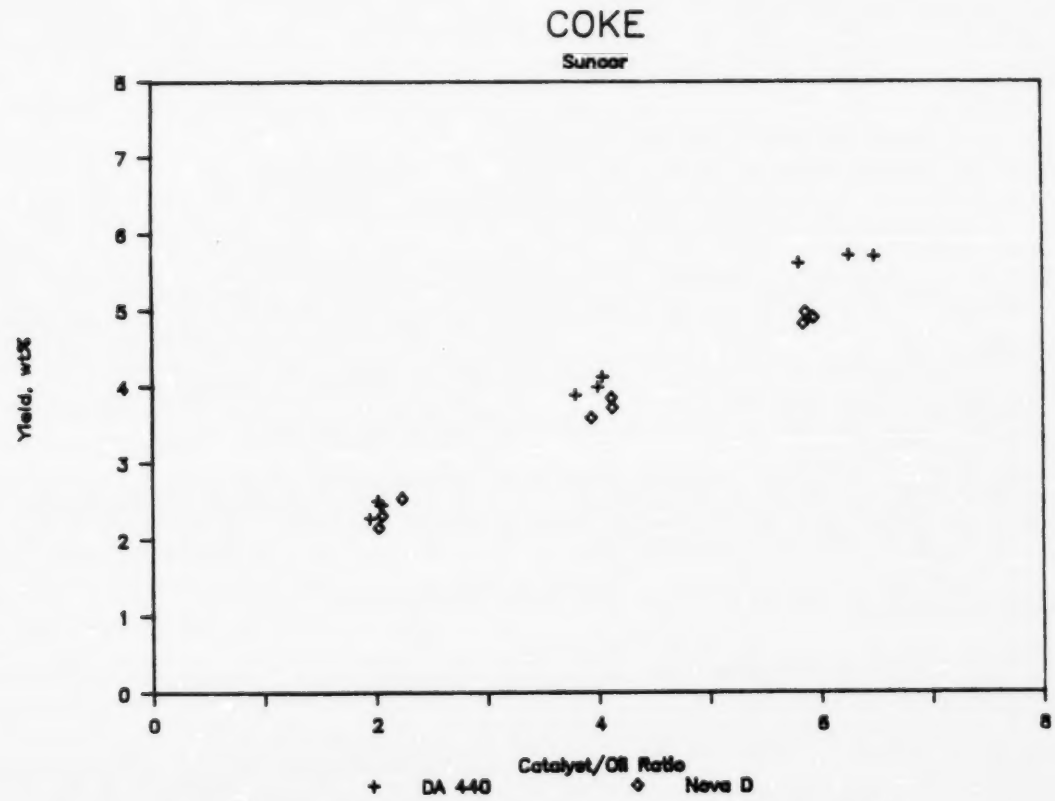

DECANT OIL
Suncor
470C
510 C
Yield, wt%
Conversion, wt%
DA 440
Nova D

Fig. 45


COKE
Suncor
Yield, wt%
0
1
2
3
4
5
6
7
8
40
50
60
70
80
470C
510C
Conversion, wt%
+ DA 440
◇ Nova D


COKE
Suncor
Yield, wt%
0
1
2
3
4
5
6
7
8
0
2
4
6
8
Catalyst/Oil Ratio
+ DA 440
◇ Nova D

CRACKING CHARACTERISTICS OF THE SHALE OIL GAS OIL

The catalytic cracking of the shale oil was completely different from the other samples. (See Tables 17 & 18 for yield profile). This was to be expected based on the work of Scherzer and McArthur and other studies of the FCC of shale oils. The analysis of the shale oil showed:

65.4 wt% crackable components
18.9 wt% refractory components
15.3 wt% polars
0.4 wt% unknown.

The compositional conversion constraint would be estimated at a maximum of 81.1 wt% if only the refractory components were considered as LCO and decant oil precursor and a minimum of 65.4 wt% if the polars and unknowns were included with the refractory components. In practice, the maximum conversion achieved for the shale oil was 44.3 wt%. Since the crackable components fraction is rich in easy to crack paraffins, it is assumed that the catalyst is being poisoned rather than having difficulty in cracking these components.

Traditionally, the deactivation of catalytic cracking catalyst by shale oils has beeen attributed to basic nitrogen compounds neutralizing the acid sites. This sample contained 4570 ppm basic nitrogen which is 15 to 45 times as much as the other four gas oils studied. The major effect of this type of catalyst deactivation appears to be:

- loss of conversion
- loss of selectivity for gasoline

The level of catalyst deactivation is also reflected in the catalyst decay constant which is two to four times greater than the four other gas oils.

With this type of deactivated system, the major variable plots normally show excellent straight line relationships. For example, the conversion vs C/O ratio plots (Figs.46 & 47) are essentially straight lines for the three reactor temperatures. As would be expected, at equivalent severity the DA-440 catalyst gives the higher feedstock conversion. At low severities the catalysts give similar conversion but as the temperature and C/O are increased DA-440 gives significantly higher feedstock conversion.

Obviously, the apparent overall rate constant for cracking is lower than for other feedstocks, while the decay constant is greater. The plot of C5+ gasoline yields vs conversion

(Figs.48 & 49) are again almost straight line relationships with no discrimination w.r.t. gasoline selectivity for either catalyst. This again is expected since deactivated catalysts are not selective to gasoline production. Also the actual gasoline yield for a given conversion is much lower than would be expected for other feedstock at equivalent conversion. Since, for the severity range studied, the other feedstock gave conversion greater than 50%, the higher conversion data was extrapolated using the kinetic model to predict C5+ gasoline yield at 50% conversion. Yield data for DA-440 was used.

Calculated C5+ Gasoline Yields at 50% Conversion

Shale Oil	28 wt%
IPL Gas Oil	44 wt%
Coleville Gas Oil	42 wt%
Suncor Gas Oil	42 wt%
Lloyd Gas Oil	38 wt%

A plot of the C3C4 yield vs conversion (Fig.50) shows that at constant conversion, higher temperature favour C3C4 production. There is no discrimination w.r.t. catalysts.

Similiar conclusions can be reached concerning the variation in dry gas make with conversion. (Fig.51). Although for consistency within this report, the dry gas make has been plotted as a function of conversion, it would be more correct to relate the dry gas yield to reactor severity. The total dry gas make is not affected by catalyst deactivation. Thus, the range of dry gas makes are comparable to those obtained when cracking the other feedstocks.

Comparison of Dry Gas Make at High Severity

DA-440 C/O Nominally 6 Reactor Temperature 510C
For comparative purposes: Net Dry Gas = Dry Gas wt% - H2S wt%

	Net Dry Gas
Shale Oil	2.08 wt%
IPL Gas Oil	1.93 wt%
Coleville Gas Oil	1.96 wt%
Suncor Gas Oil	1.91 wt%
Lloyd Gas Oil	1.99 wt%

It is of interest to note that the hydrogen yield for the shale oil is less than for the other gas oils and that the ethane/ethylene ratio is greater than obtained when cracking the other gas oils.

The shale oil contains 27 wt% of 343C minus materials while the LCO yield in the cracked product averaged approximately 30 wt%. There was a marginal decline in LCO make with conversion at 510C with DA-440 catalyst but generally there was little change in LCO yield with conversion. (Fig.52)

The plot of decant oil yield vs conversion (Fig.53) is a straight line as is required if the LCO yield is essentially constant. The coke selectivity plots (Fig.54) also fit on straight lines for the equal temperature data points. This is to be expected since the C/O ratio vs conversion plots were also straight lines with temperature.

The fact that the DA-440 shows improved selectivity over the Nova D catalyst especially at the higher temperatures simply reflects the fact that DA-440 is the more active catalyst. Therefore, a particular conversion will be achieved using DA-440 at a lower C/O ratio, and hence lower coke make than Nova D.

Table 17

MICROACTIVITY TEST RESULTS USING
DA 440 EQUILIBRIUM CATALYST AND
SHALE OIL GAS OIL

RUN NO.	90	92	94	96	98	100	102	104	106
Reactor TempC	470	470	470	490	490	490	510	510	510
WHSV HR-1	19.10	19.90	19.60	18.70	19.00	19.80	19.10	17.70	19.20
C/O	2.05	3.93	5.92	2.07	4.03	5.86	2.05	4.31	5.85
H2	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.02
H2S	0.09	0.15	0.18	0.10	0.15	0.18	0.13	0.18	0.21
C1	0.13	0.20	0.25	0.24	0.36	0.42	0.40	0.57	0.69
C2	0.17	0.27	0.36	0.29	0.44	0.50	0.44	0.63	0.74
C2-	0.13	0.22	0.29	0.21	0.35	0.43	0.34	0.52	0.63
Total Dry Gas	0.52	0.85	1.09	0.84	1.31	1.54	1.32	1.91	2.29
C3	0.29	0.50	0.73	0.41	0.71	0.84	0.55	0.87	1.06
C3-	0.53	0.98	1.41	0.78	1.39	1.73	1.00	1.75	2.21
i-C4	0.66	1.30	1.93	0.76	1.44	2.00	0.80	1.64	2.20
n-C4	0.22	0.43	0.62	0.30	0.54	0.69	0.37	0.66	0.84
C4-	0.55	1.06	1.54	0.82	1.41	1.85	1.02	1.81	2.29
Total C3C4	2.25	4.27	6.23	3.07	5.49	7.11	3.74	6.73	8.60
i-C5	0.72	1.46	2.19	0.88	1.64	2.31	0.91	1.91	2.52
n-C5	0.10	0.18	0.33	0.16	0.31	0.34	0.21	0.31	0.44
C5-	0.46	0.88	1.41	0.81	1.29	1.45	0.85	1.58	1.88
Total C5	1.28	2.52	3.93	1.85	3.24	4.10	1.97	3.80	4.84
C5-216C	10.05	16.35	23.23	12.34	18.69	24.70	14.36	22.72	27.07
C6-216C	8.77	13.83	19.30	10.49	15.45	20.60	12.39	18.92	22.23
216-343C	30.07	29.73	29.26	30.19	30.47	29.20	31.72	29.99	28.98
343C-E.P.	53.78	43.83	33.22	50.61	39.26	31.15	46.02	33.59	26.75
Coke	3.32	4.97	6.96	2.96	4.79	6.32	2.84	5.08	6.30
Conversion	16.14	26.44	37.52	19.20	30.27	39.65	22.25	36.41	44.26
Material Balance	100.10	99.50	100.70	100.00	100.80	101.60	99.93	100.50	102.50

Table 18

MICROACTIVITY TEST RESULTS USING
NOVA B EQUILIBRIUM CATALYST AND
SHALE OIL GAS OIL

RUN NO.	89	91	93	95	97	99	101	103	105
Reactor TempC	470	470	470	490	490	490	510	510	510
WHSV HR-1	18.90	18.90	19.40	18.60	18.60	19.40	18.90	19.00	19.00
C/O	2.05	4.10	5.96	2.08	4.12	5.97	2.05	4.03	5.92
H2	0.00	0.02	0.01	0.00	0.02	0.02	0.01	0.02	0.03
H2S	0.09	0.14	0.18	0.10	0.11	0.20	0.13	0.16	0.19
C1	0.17	0.23	0.26	0.26	0.37	0.47	0.38	0.56	0.72
C2	0.21	0.32	0.37	0.32	0.44	0.58	0.42	0.62	0.76
C2-	0.14	0.22	0.27	0.21	0.31	0.41	0.29	0.47	0.60
Total Dry Gas	0.61	0.93	1.09	0.89	1.25	1.68	1.23	1.83	2.30
C3	0.31	0.54	0.67	0.42	0.61	0.85	0.53	0.71	0.99
C3-	0.52	0.93	1.25	0.71	1.18	1.66	0.97	1.40	2.01
i-C4	0.66	1.22	1.67	0.67	1.24	1.93	0.80	1.21	1.93
n-C4	0.23	0.42	0.54	0.29	0.49	0.71	0.36	0.54	0.79
C4-	0.57	1.03	1.37	0.78	1.26	1.82	1.00	1.48	2.14
Total C3C4	2.29	4.14	5.50	2.87	4.78	6.97	3.66	5.34	7.86
i-C5	0.65	1.33	1.85	0.73	1.37	2.09	0.92	1.30	2.12
n-C5	0.11	0.22	0.28	0.16	0.21	0.39	0.22	0.25	0.42
C5-	0.43	0.93	1.34	0.60	1.40	1.74	0.86	1.34	1.87
Total C5	1.19	2.48	3.47	1.49	2.98	4.22	2.00	2.89	4.41
C5-216C	9.75	15.80	20.54	11.60	17.84	22.53	13.85	19.34	24.45
C6-216C	8.56	13.32	17.07	10.11	14.86	18.31	11.85	16.45	20.04
216-343C	30.32	30.23	29.83	31.08	30.67	29.78	30.74	32.49	30.69
343C-E.P.	53.62	43.92	36.04	50.43	40.44	33.06	47.36	36.43	28.56
Coke	3.40	5.00	7.01	3.11	5.03	5.98	3.15	4.56	6.12
Conversion	16.06	25.85	34.13	18.49	28.89	37.17	21.89	31.08	40.75
Material Balance	100.20	99.60	100.50	100.00	100.50	99.30	98.80	100.80	100.50

Fig. 46 Shale Oil & DA 440

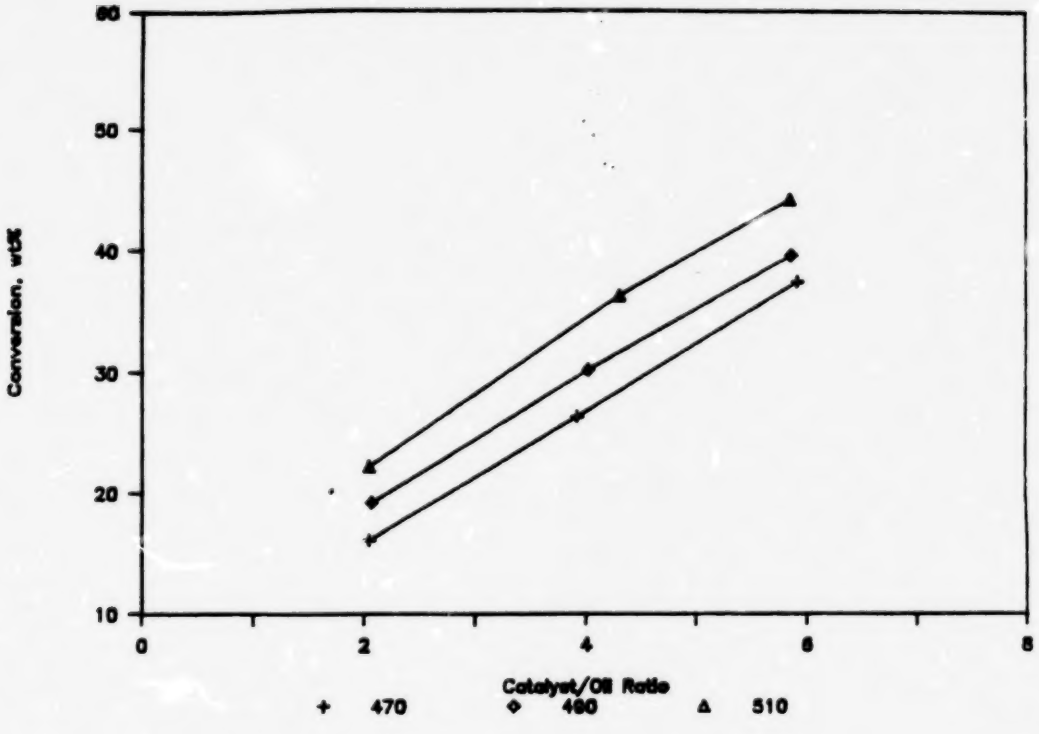


Fig. 47 Shale Oil & Nova D

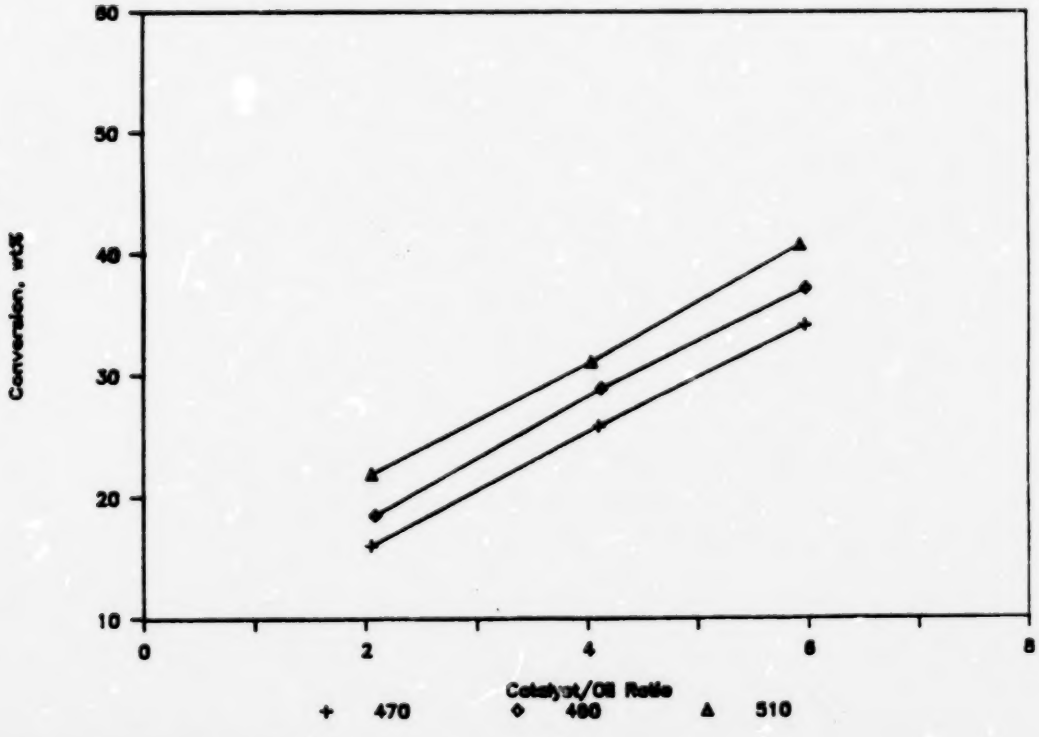


Fig. 48

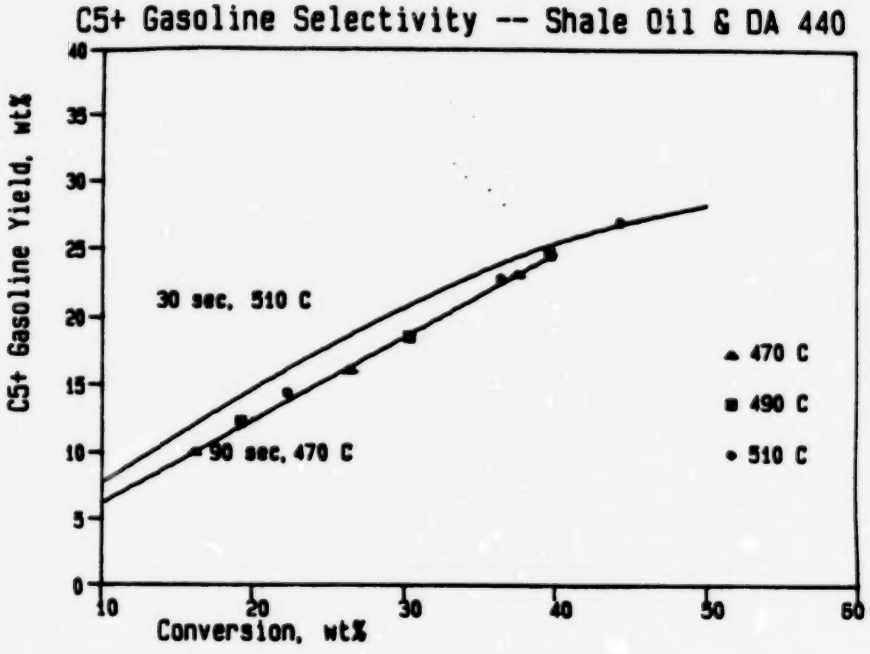

C5+ Gasoline Selectivity -- Shale Oil & DA 440
C5+ Gasoline Yield, wt%
Conversion, wt%
30 sec, 510 C
90 sec, 470 C
470 C
490 C
510 C
0
5
10
15
20
25
30
35
40
10
20
30
40
50
60

Fig. 49

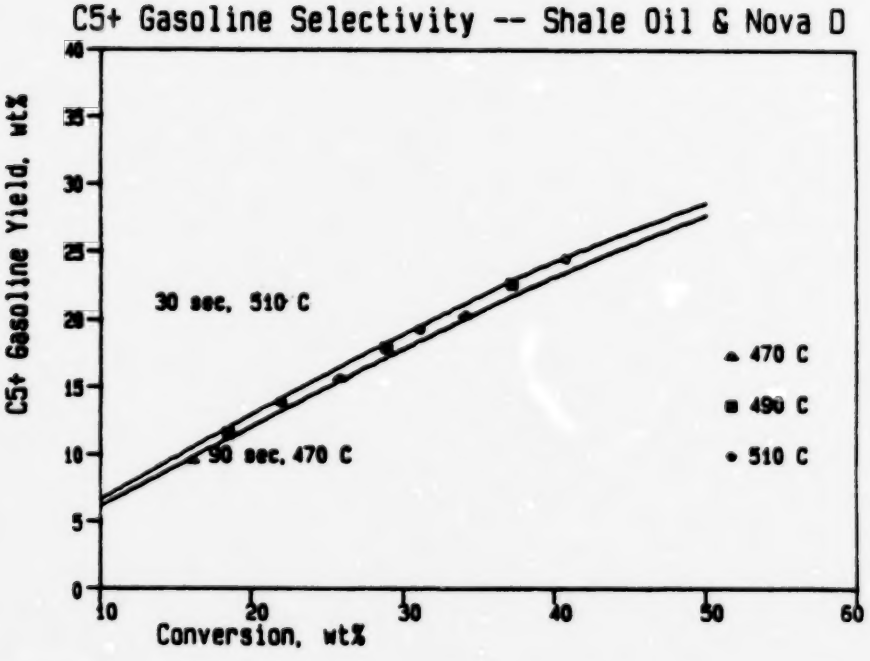

C5+ Gasoline Selectivity -- Shale Oil & Nova D
C5+ Gasoline Yield, wt%
Conversion, wt%
30 sec, 510 C
90 sec, 470 C
470 C
490 C
510 C
0
5
10
15
20
25
30
35
40
10
20
30
40
50
60

Fig. 51

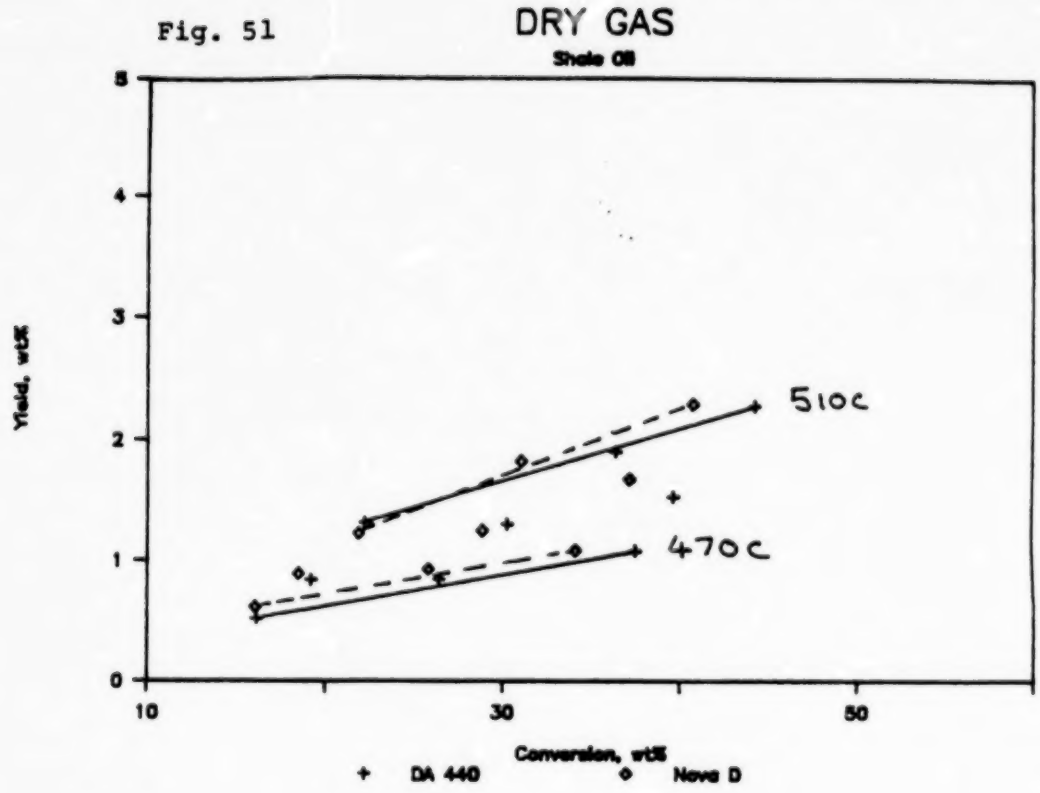

DRY GAS
Shale Oil
Yield, wt%
0
1
2
3
4
5
10
30
50
Conversion, wt%
510C
470C
DA 440
Nova D

Fig. 50

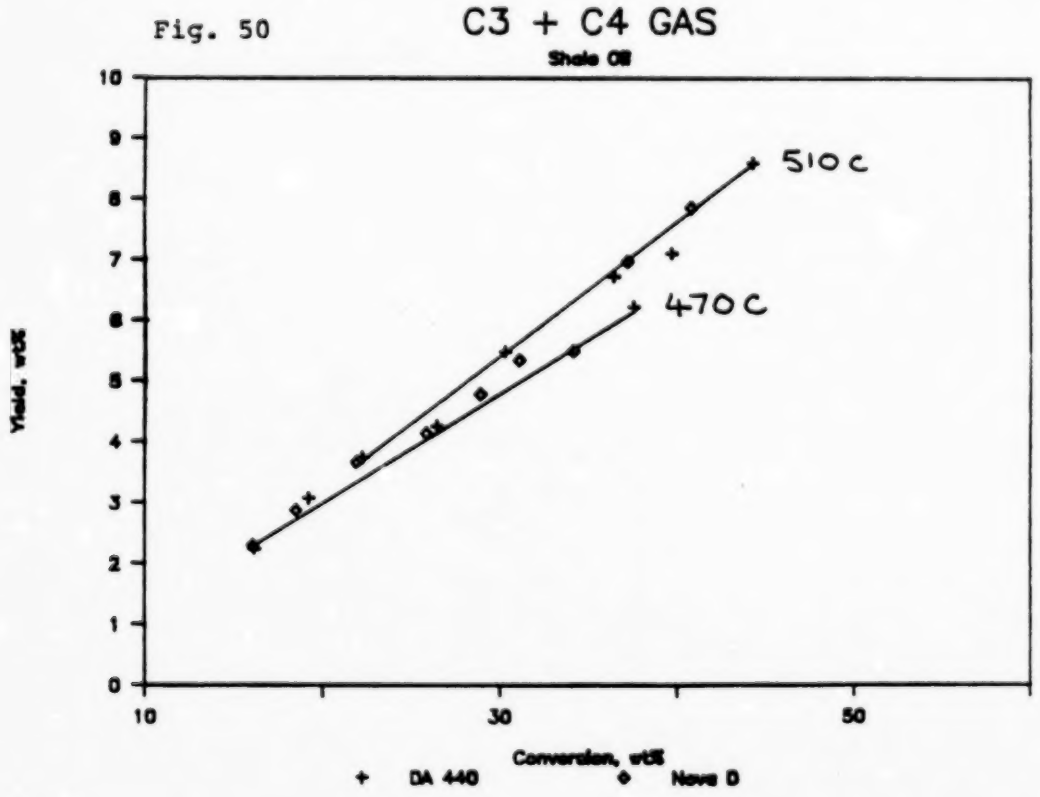

C3 + C4 GAS
Shale Oil
Yield, wt%
0
1
2
3
4
5
6
7
8
9
10
10
30
50
Conversion, wt%
510C
470C
DA 440
Nova D

Fig. 52

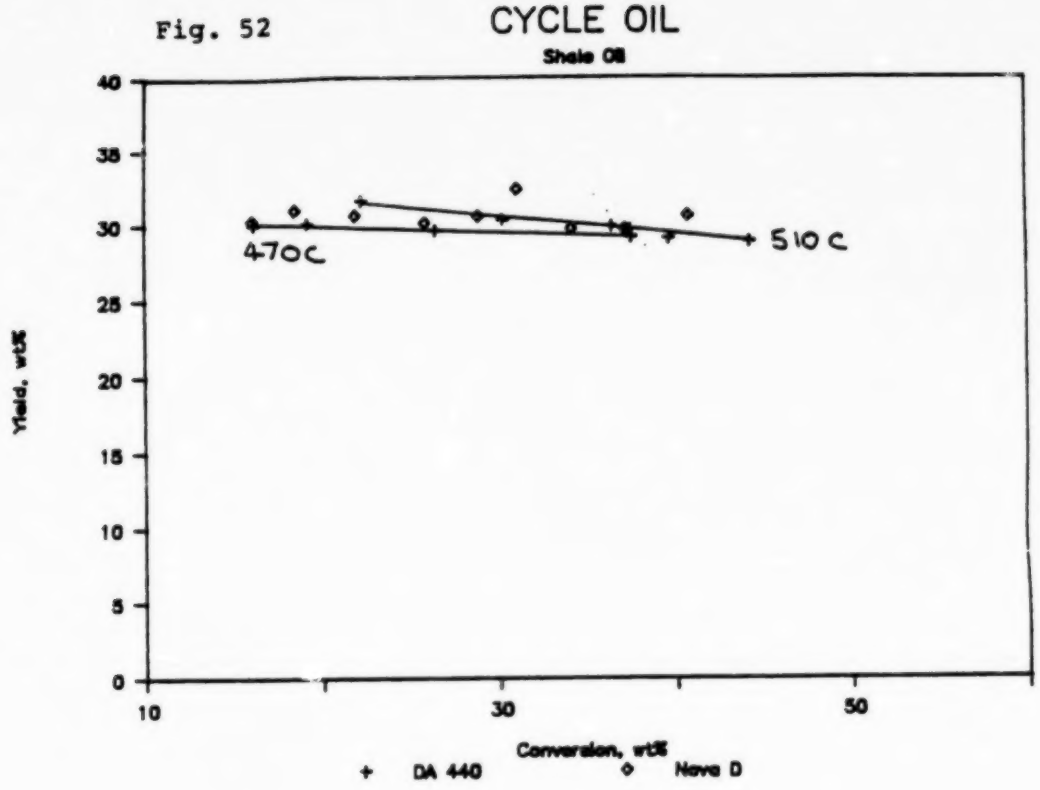

CYCLE OIL
Shale Oil
470C
510C
Yield, wt%
Conversion, wt%
DA 440
Nova D

Fig. 53

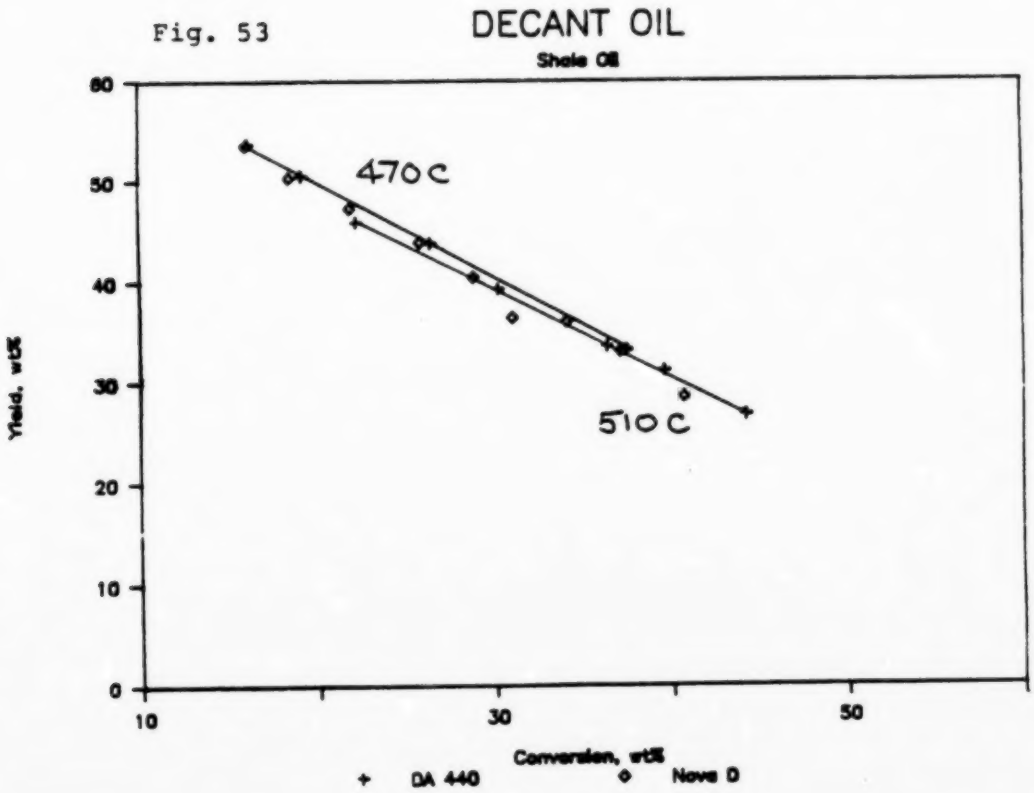
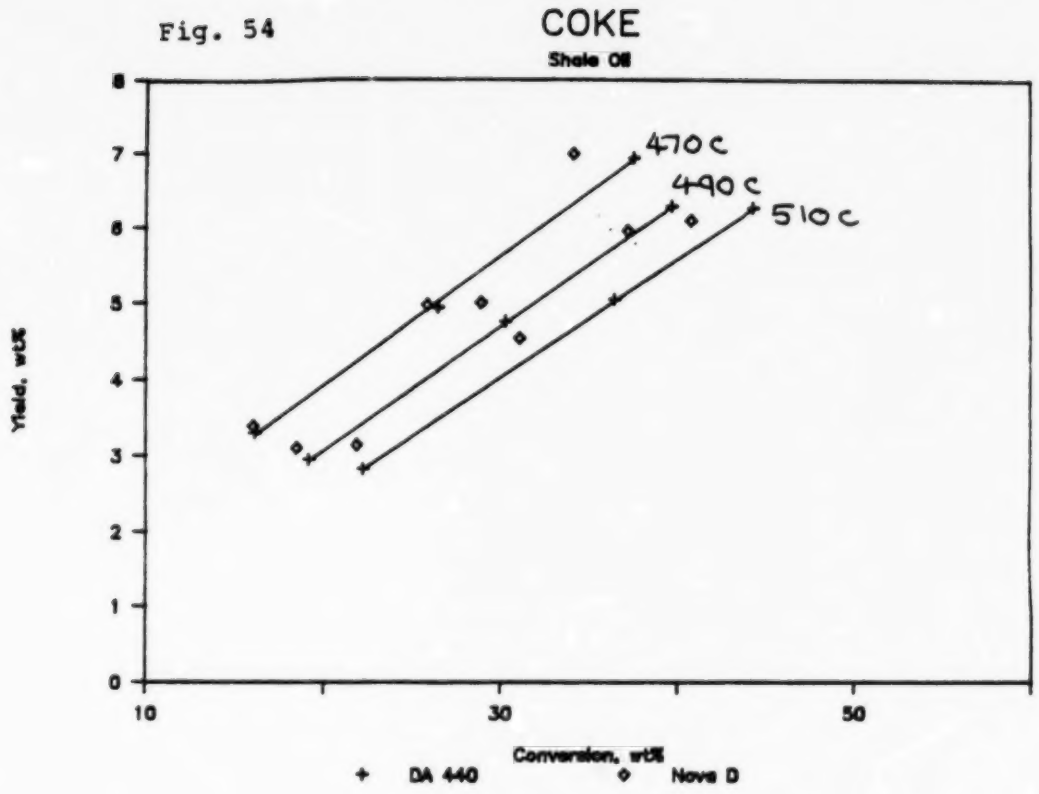
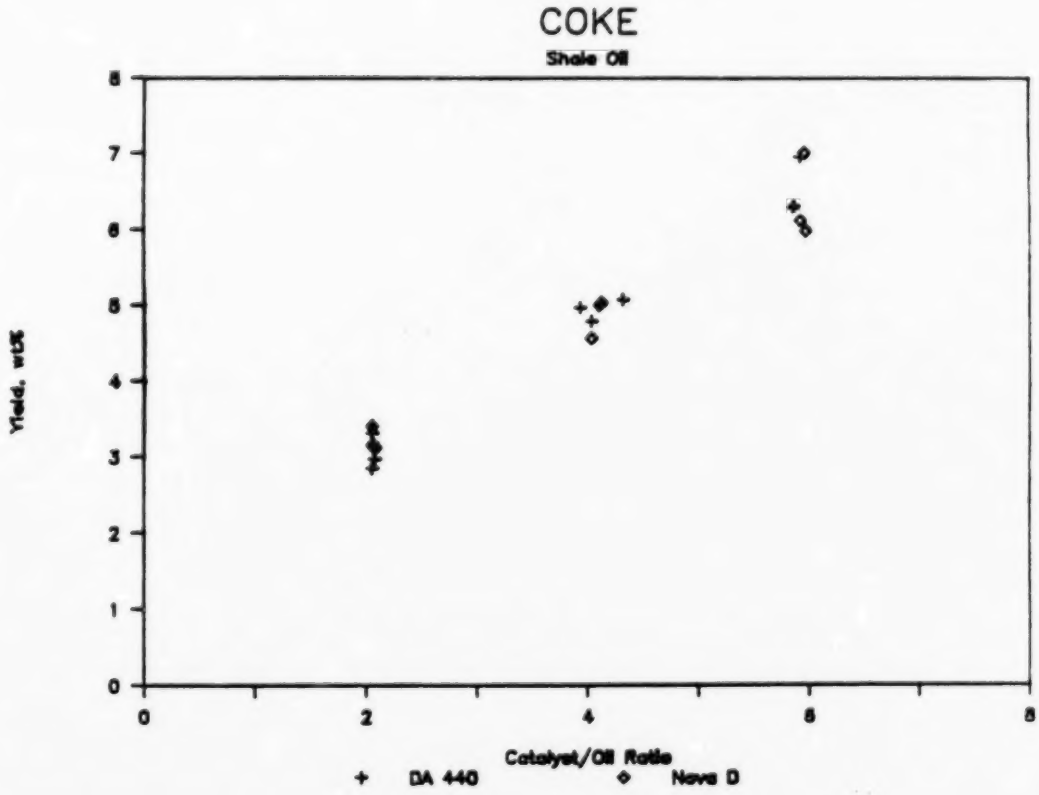

DECANT OIL
Shale Oil
470C
510C
Yield, wt%
Conversion, wt%
DA 440
Nova D

Fig. 54


COKE
Shale Oil
470 C
490 C
510 C
Yield, wt%
Conversion, wt%
10
30
50
0
1
2
3
4
5
6
7
8
DA 440
Nova D


COKE
Shale Oil
Yield, wt%
Catalyst/Oil Ratio
0
2
4
6
8
0
1
2
3
4
5
6
7
8
DA 440
Nova D

CRACKING CHARACTERISTICS OF CANMET FR-3 GAS OIL

MAT runs using CANMET gas oil were added near the end of the contract to replace the Special MAT runs.

Nine MAT tests were carried out under this contract, and the other tests were carried out under a separate contract. For convenience, all the results are included here. The inspection and composition reported for this gas oil, reported in Tables 1 & 2 were provided by CANMET. The HRMS analysis reported for this gas oil differs from the LRMS analysis carried out on the other five gas oils. Separation into saturates, aromatics and polars is not required for the HRMS methods. Therefore, quantitative data on the concentration of polar is not available.

Because of the anticipated need to operate at severe conditions, the maximum operating temperature was increased to 530C and the MAT runs at 470C were eliminated.

Based on the composition and inspections, the CANMET gas oil was the lowest quality feedstock evaluated in this contract. It contained only 52.8 wt% crackable components and the compositional constraint to conversion was also calculated at 52.8%. In addition, the oil contained a high concentration of nitrogen compounds.

The plot of conversion vs C/O ratio (Figs. 55 & 56) shows that the compositional conversion constraint was exceeded when operating at high C/O and high reactor temperatures using the DA-440 catalyst. The conversion plots are more similar to the shale oil than the other feedstocks, showing a relatively steep increase of conversion with C/O roughly parallel straight lines for the plots at different reactor temperatures. At low C/O ratios, the two feedstocks give equivalent conversions. At higher C/O ratio, CANMET gives higher conversions. As expected, the DA-440 catalyst is significantly more active when converting the CANMET gas oil at all severities. Kinetic data obtained from the MAT runs show that there is a very high catalyst decay rate associated with cracking this feedstock over both catalyst (see Tables 7 & 8). The model shows that the catalyst decay constant is greater for the CANMET feed than for the shale oil. As found for the majority of feedstocks, the catalyst decay rate increases with decreasing temperatures, suggesting that adsorption phenomena may be more important than coke formation in governing catalyst decay.

The C5 gasoline selectivity plots (Figs.57 & 58) show no sign of overcracking. In fact, the large increase in gasoline

yield when increasing the C/O from 4 to 6 at 530C, combined with the slope of the conversion plots, would suggest that additional conversion and gasoline are available under more severe conditions or with more active/resistant catalyst. In fact, it appears for this feedstock that the compositional conversion constraint may be higher than has been estimated.

Inspection of the C6+ gasoline yields shows that at all temperatures, increasing the C/O ratio from 4 to 6 increases the C6+ gasoline yield. The only sign of overcracking is the decrease in C6+ gasoline with temperature at the high C/O ratio for the DA-440 catalyst.

Variation in C6+ Gasoline Yield with Temperature

Run No.	192	198	196
C/O Ratio	5.83	6.06	5.91
Temperature C	490	510	530
C6+ Gasoline wt%	27.08	26.14	26.43
C5+ Gasoline wt%	30.80	31.51	32.05

The gasoline selectivity plots (Figs. 57 & 58) show that the two catalysts are equivalent for this feedstock. The fact that the increased activity of the DA-440 catalyst does not favour additional gasoline selectivity is another sign of significant deactivation. However, it should be noted that at equivalent severity, the DA-440 catalyst will produce more gasoline.

Like the shale oil, this feedstock showed a poor selectivity to gasoline. This was attributed to two interrelated factors:

- catalyst poisoning reducing gasoline selectivity
- the need to operate at high severity to achieve some conversion. High severity favours gas and coke production, hence reducing gasoline selectivity.

Although the CANMET feedstock was a much more refractory feedstock than the shale oil, the gasoline selectivity plots for the two feedstocks are almost identical up to a conversion of 40%.

The earlier comparison of optimum projected yields at 50% conversion is updated here:

Calculated C5+ Gasoline Yields at 50% Conversion

CANMET gas oil	31 wt%
Shale oil	28 wt%
IPL gas oil	44 wt%
Coleville gas oil	42 wt%
Suncor gas oil	42 wt%
Lloyd gas oil	38 wt%

It is surprising that the CANMET feed is more selective to gasoline than the Shale oil at 50% conversion based on compositional considerations.

The plot of the C3C4 yield vs conversion is shown in Fig.59. The normal temperature effects are noted i.e. at equivalent conversion, the higher temperature operation produces more C3C4, and the two catalysts have equivalent selectivities. Similar conclusions can be made for the dry gas yields (see Fig.60). As discussed earlier, the total "net" dry gas make (excluding H2S) is more dependent on operating severity than conversion. For this feedstock using DA-440, a C/O of 6.06 and a reactor temperature of 510C, the "net" dry gas make was 1.93 wt%. This is in line with the net dry gas makes for the other five feedstocks reported earlier.

The CANMET gas oil contains 24 wt% of 343C minus material while the LCO yield from the MAT runs averaged 27 to 28 wt% There was a marginal decline in light cycle oil yield with conversion when the reactor was operated at 530C. At lower reactor temperatures, there was little change in LCO yield with conversion. (Fig.61)

The decant oil yield decline with conversion is essentially a straight line with little temperature discrimination (see Fig. 62).

The coke selectivity plots are a series of straight lines (Fig. 63) quite similar to the data obtained for the shale oil. When the two plots are superimposed, the coke make line at 510C for CANMET is between the 490C and 510C lines for the shale oil.

The similarity between conversion, gasoline make and coke make for these quite dissimilar feedstocks, is somewhat surprising and certainly indicates the levelling effect of catalyst deactivation.

Table 19

MICROACTIVITY TEST RESULTS USING
DA 440 EQUILIBRIUM CATALYST AND
CANMET FR3 GAS OIL

RUN NO.	180	178	192	174	172	198	188	186	184	196
Reactor TempC	490	490	490	510	510	510	530	530	530	530
WHSV HR-1	20.90	23.20	23.50	21.60	21.40	22.60	21.20	22.30	22.80	23.2
C/O	2.04	3.66	5.83	1.86	3.50	6.06	2.09	3.98	5.66	5.91
H2	0.04	0.07	0.06	0.06	0.09	0.08	0.07	0.08	0.09	0.1
H2S	0.50	0.94	1.03	0.45	0.85	1.38	0.75	1.01	1.22	1.33
C1	0.12	0.25	0.26	0.23	0.33	0.59	0.41	0.59	0.77	0.82
C2	0.15	0.29	0.34	0.25	0.35	0.59	0.41	0.64	0.72	0.78
C2-	0.16	0.32	0.40	0.25	0.36	0.67	0.39	0.66	0.76	0.82
Total Dry Gas	0.97	1.87	2.09	1.24	1.98	3.31	2.03	2.98	3.56	3.85
C3	0.27	0.60	0.78	0.37	0.63	1.21	0.55	0.92	1.27	1.38
C3-	0.73	1.59	1.97	0.98	1.63	3.05	1.36	2.33	2.94	3.23
i-C4	0.67	1.57	2.15	1.00	1.45	3.06	0.99	1.91	2.65	2.92
n-C4	0.19	0.44	0.59	0.24	0.44	0.91	0.37	0.63	0.89	0.96
C4-	0.68	1.54	1.96	0.91	1.58	2.99	1.27	2.28	2.81	3.17
Total C3C4	2.54	5.74	7.45	3.50	5.73	11.22	4.54	8.07	10.56	11.66
i-C5	0.74	1.59	2.21	0.82	1.52	3.19	1.02	1.90	2.75	3.08
n-C5	0.09	0.20	0.23	0.10	0.18	0.31	0.18	0.29	0.35	0.46
C5-	0.49	1.02	1.28	0.72	1.13	1.87	0.86	1.51	1.77	2.08
Total C5	1.32	2.81	3.72	1.64	2.83	5.37	2.06	3.70	4.87	5.62
C5-216C	13.99	21.82	30.80	14.52	22.65	31.51	17.47	26.16	30.47	32.05
C6-216C	12.67	19.01	27.08	12.88	19.82	26.14	15.41	22.46	25.60	26.43
216-343C	27.51	27.82	28.96	27.67	27.66	25.50	28.65	27.52	25.89	24.88
343C-E.P.	52.16	38.31	23.91	50.51	37.76	21.59	44.35	30.22	22.91	20.67
Coke	2.83	4.43	6.80	2.54	4.23	6.87	2.94	5.04	6.60	6.89
Conversion	20.33	33.87	47.13	21.82	34.57	52.91	27.00	42.26	51.20	54.45
Material Balance	100.57	98.50	101.42	99.65	99.53	98.34	98.85	98.87	98.60	97.08

Table 20

MICROACTIVITY TEST RESULTS USING
NOVA B EQUILIBRIUM CATALYST AND
CANMET FR3 GAS OIL

RUN NO.	179	177	193	173	171	191	189	187	195
Reactor TempC	490	490	490	510	510	510	530	530	530
WHSV HR-1	21.30	21.80	23.20	21.10	21.30	23.20	21.00	22.50	23.00
C/O	2.00	3.66	5.90	1.77	3.37	5.71	2.12	3.97	5.94
H2	0.07	0.12	0.09	0.10	0.13	0.12	0.09	0.15	0.16
H2S	0.55	0.75	0.97	0.54	0.72	1.02	0.66	1.00	1.13
C1	0.15	0.20	0.30	0.22	0.32	0.47	0.38	0.68	0.73
C2	0.18	0.25	0.36	0.23	0.37	0.52	0.38	0.66	0.75
C2-	0.17	0.25	0.38	0.20	0.35	0.54	0.32	0.62	0.73
Total Dry Gas	1.12	1.57	2.10	1.29	1.89	2.67	1.83	3.11	3.50
C3	0.30	0.45	0.74	0.32	0.52	0.85	0.47	0.89	1.12
C3-	0.73	1.11	1.84	0.77	1.29	2.09	1.10	2.14	2.67
i-C4	0.65	1.08	1.94	0.58	1.09	1.94	0.77	1.62	2.21
n-C4	0.20	0.32	0.55	0.19	0.34	0.57	0.29	0.57	0.72
C4-	0.70	1.09	1.88	0.72	1.27	2.17	1.07	2.19	2.69
Total C3C4	2.58	4.05	6.95	2.58	4.51	7.62	3.70	7.41	9.41
i-C5	0.67	1.12	1.94	0.62	1.11	2.00	0.80	1.60	2.24
n-C5	0.10	0.15	0.20	0.11	0.19	0.27	0.15	0.22	0.33
C5-	0.56	0.82	1.30	0.38	0.74	1.93	0.89	1.41	1.82
Total C5	1.33	2.09	3.44	1.11	2.04	4.20	1.84	3.23	4.39
C5-216C	12.23	19.05	28.27	12.25	19.07	27.51	15.80	23.05	29.47
C6-216C	10.90	16.96	24.83	11.14	17.03	23.31	13.96	19.82	25.08
216-343C	27.83	28.50	29.33	27.99	28.58	28.13	28.70	27.63	27.39
343C-E.P.	53.46	42.53	27.00	53.48	41.95	27.66	46.90	33.84	23.44
Coke	2.77	4.30	6.36	2.41	4.00	6.40	3.05	4.97	6.79
Conversion	18.71	28.98	43.67	18.54	29.47	44.20	24.40	38.53	49.17
Material Balance	99.81	99.97	101.75	99.58	99.78	100.53	100.06	98.99	100.04

Fig. 55

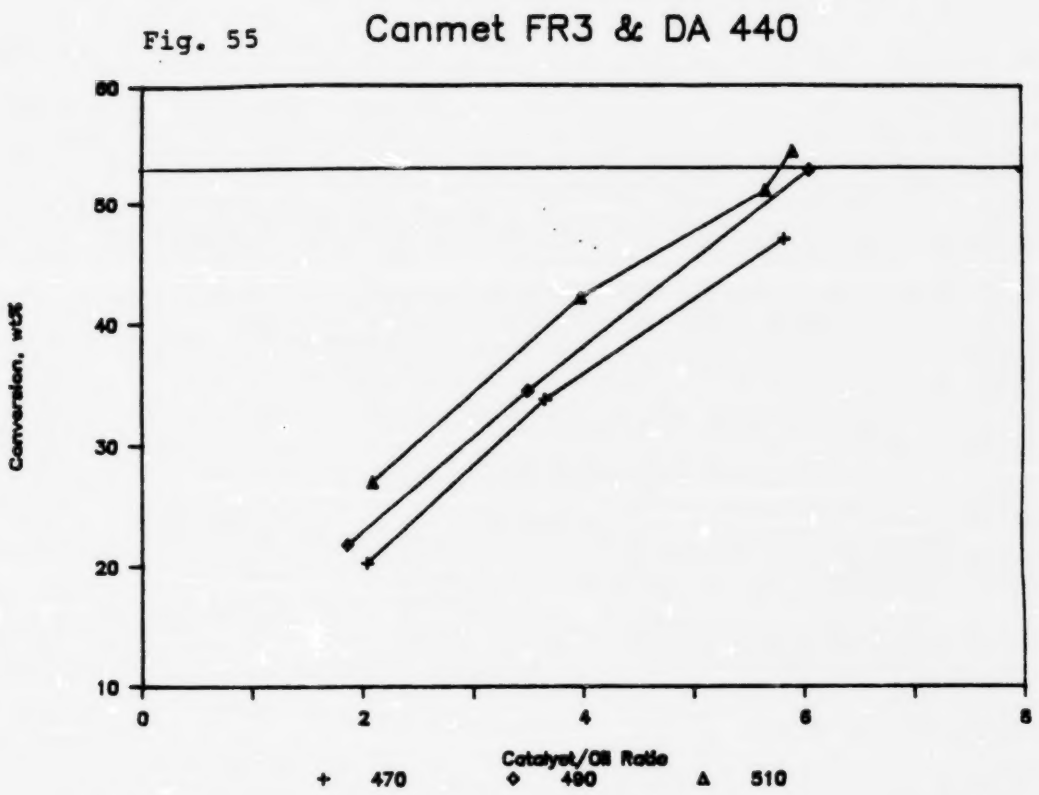

Canmet FR3 & DA 440
Conversion, wt%
60
50
40
30
20
10
0
2
4
6
8
Catalyst/Oil Ratio
+ 470
◇ 490
△ 510

Fig. 56

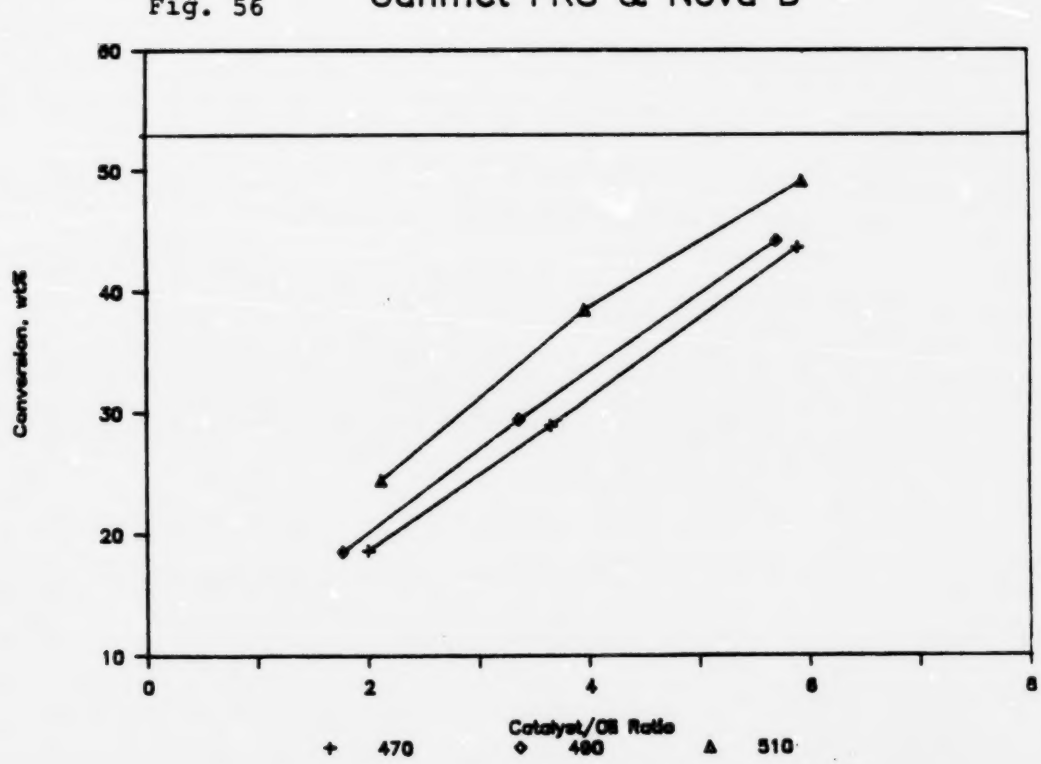

Canmet FR3 & Nova D
Conversion, wt%
60
50
40
30
20
10
0
2
4
6
8
Catalyst/Oil Ratio
+ 470
◇ 490
△ 510

Fig. 57

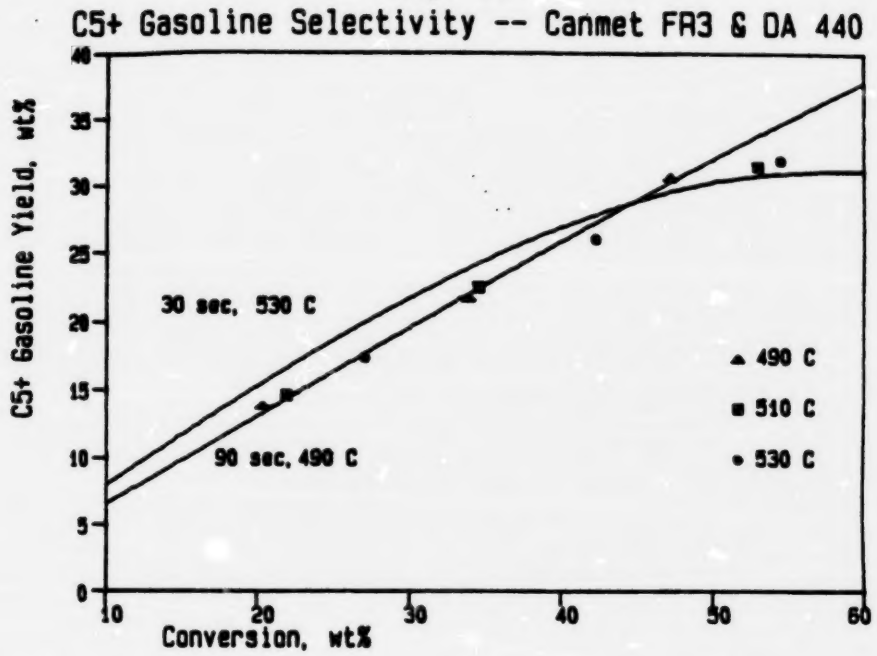

C5+ Gasoline Selectivity -- Canmet FR3 & DA 440
C5+ Gasoline Yield, wt%
Conversion, wt%
30 sec, 530 C
90 sec, 490 C
490 C
510 C
530 C

Fig. 58

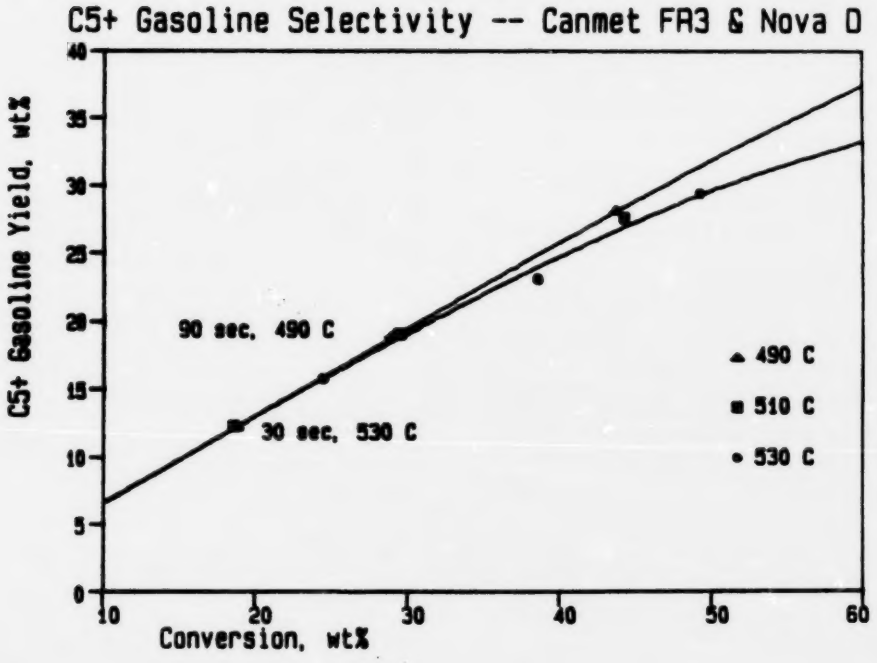

C5+ Gasoline Selectivity -- Canmet FR3 & Nova D
C5+ Gasoline Yield, wt%
Conversion, wt%
90 sec, 490 C
30 sec, 530 C
490 C
510 C
530 C

Fig. 60

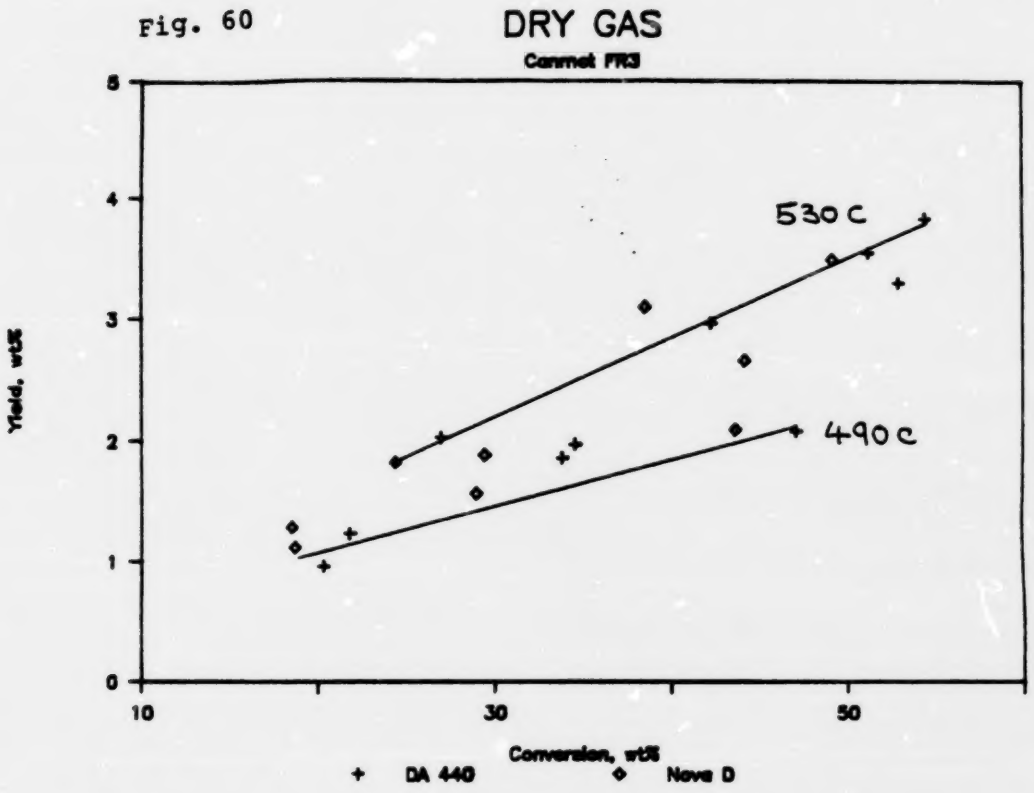

DRY GAS
Canmet FR3
530 C
490 C
Yield, wt%
Conversion, wt%
10
30
50
0
1
2
3
4
5
DA 440
Nova D

Fig. 59

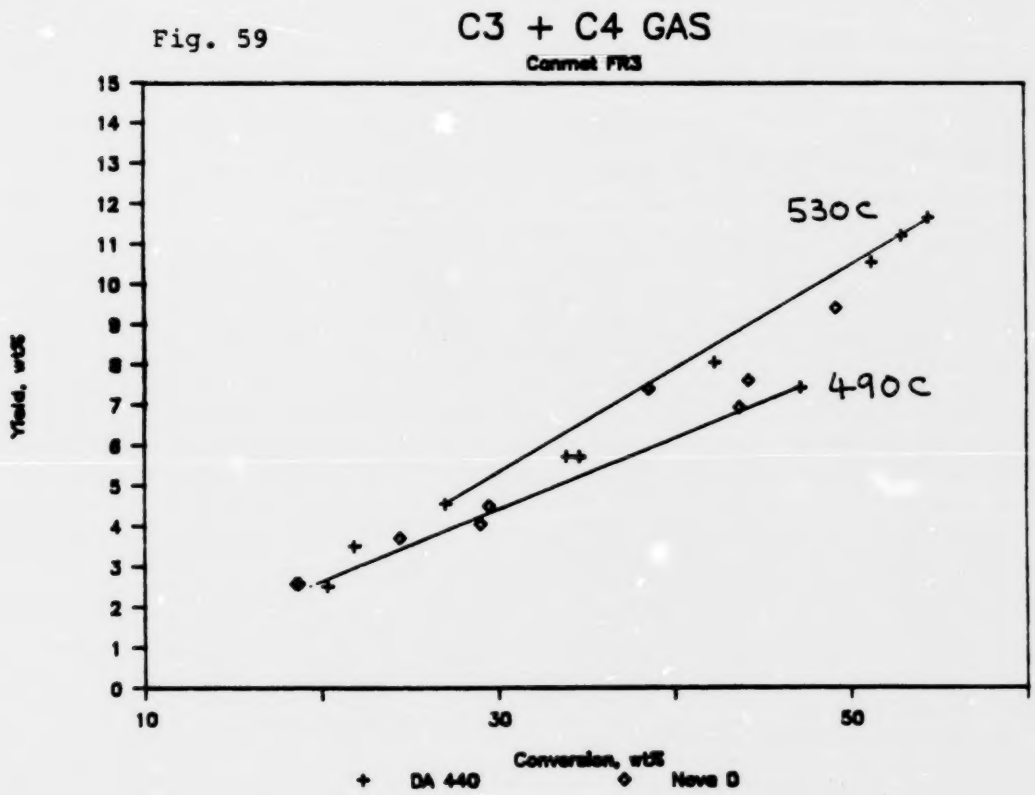

C3 + C4 GAS
Canmet FR3
530C
490C
Yield, wt%
Conversion, wt%
10
30
50
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
DA 440
Nova D

Fig. 61

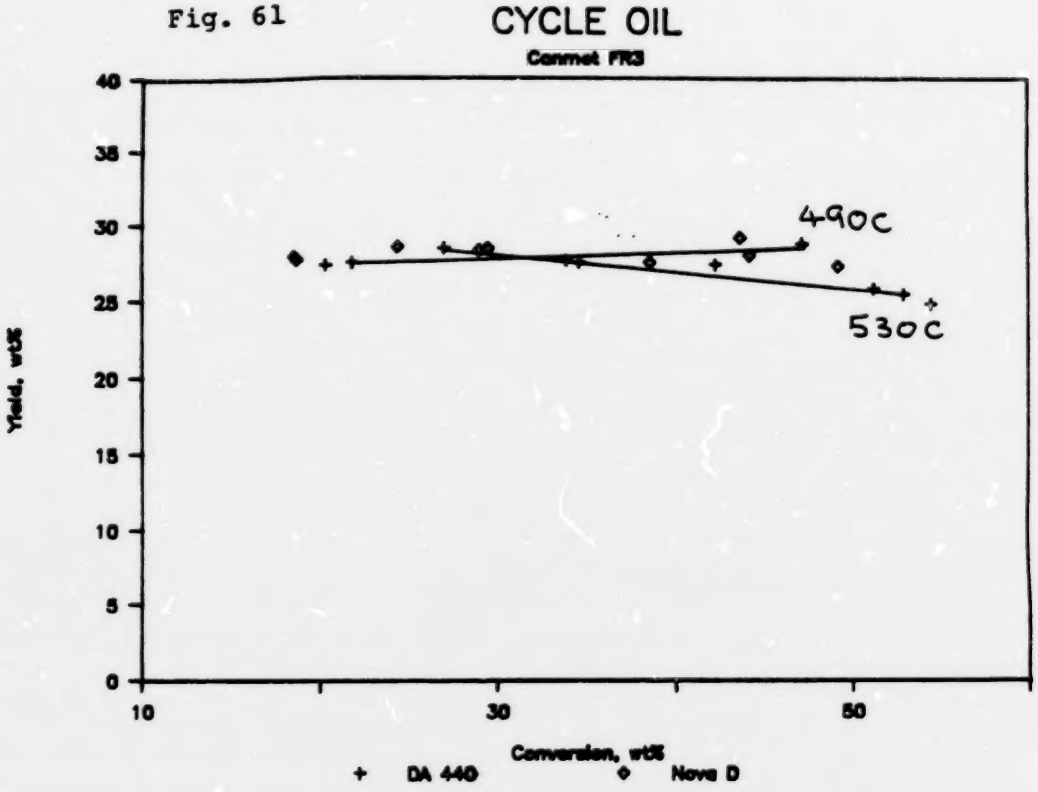

CYCLE OIL
Canmet FR3
Yield, wt%
40
35
30
25
20
15
10
5
0
10
30
50
Conversion, wt%
490c
530c
DA 440
Nova D

Fig. 62

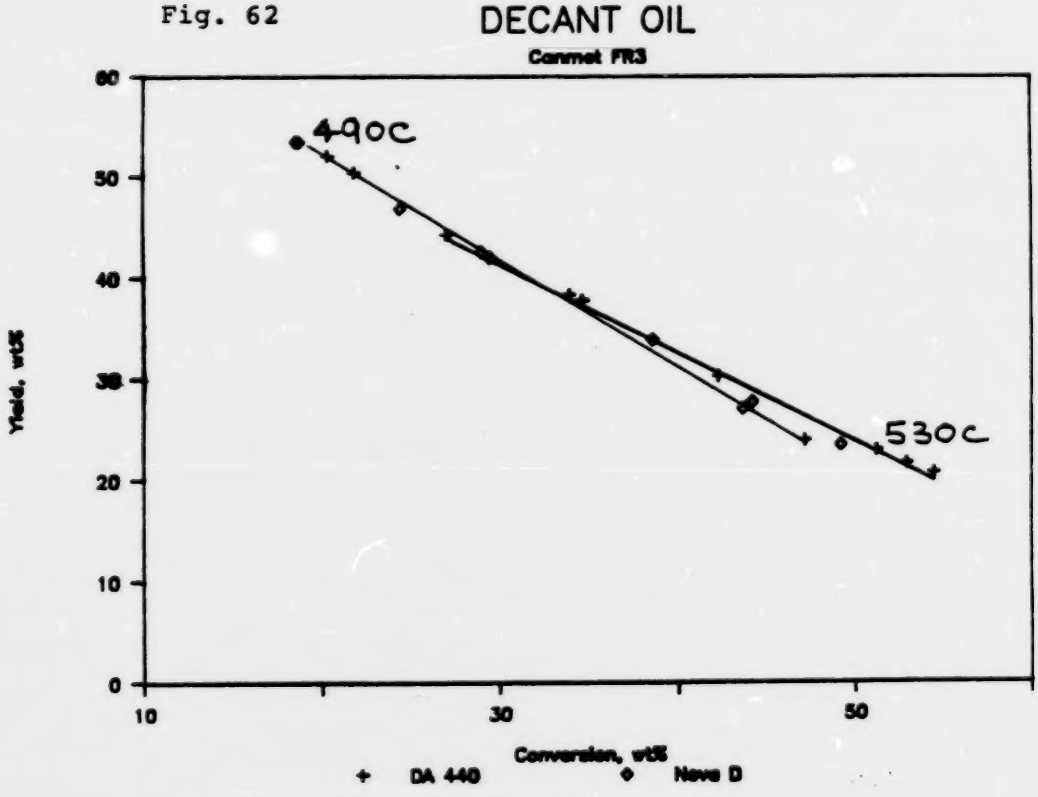
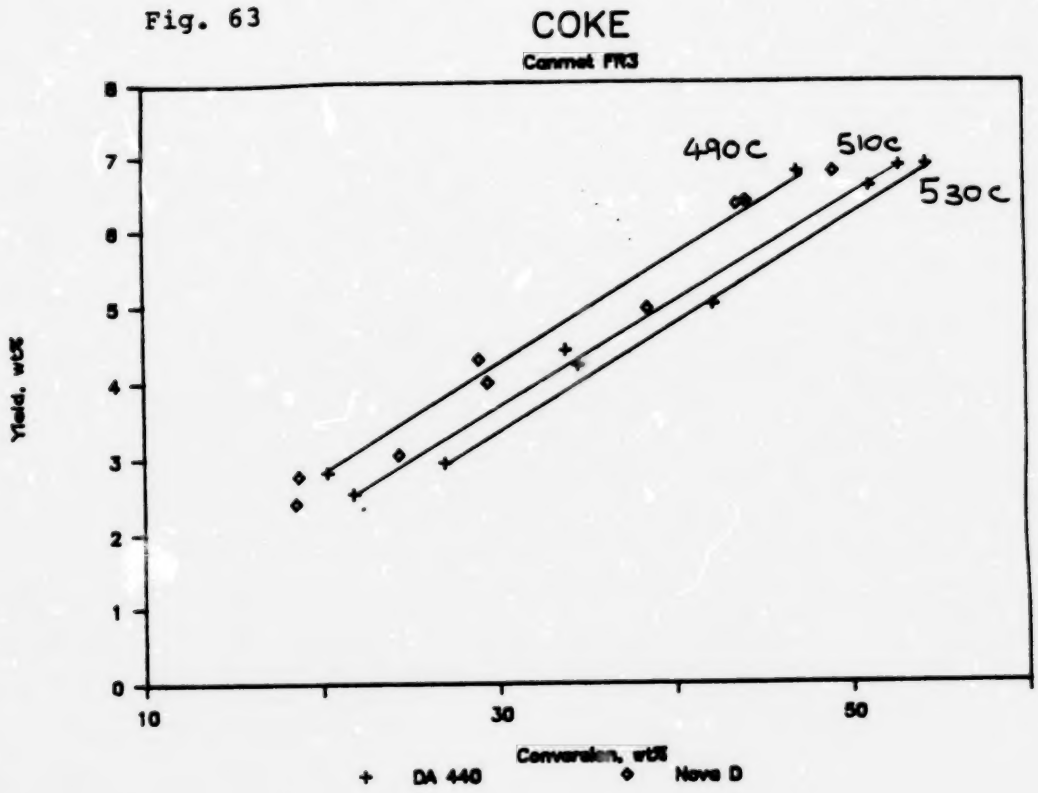
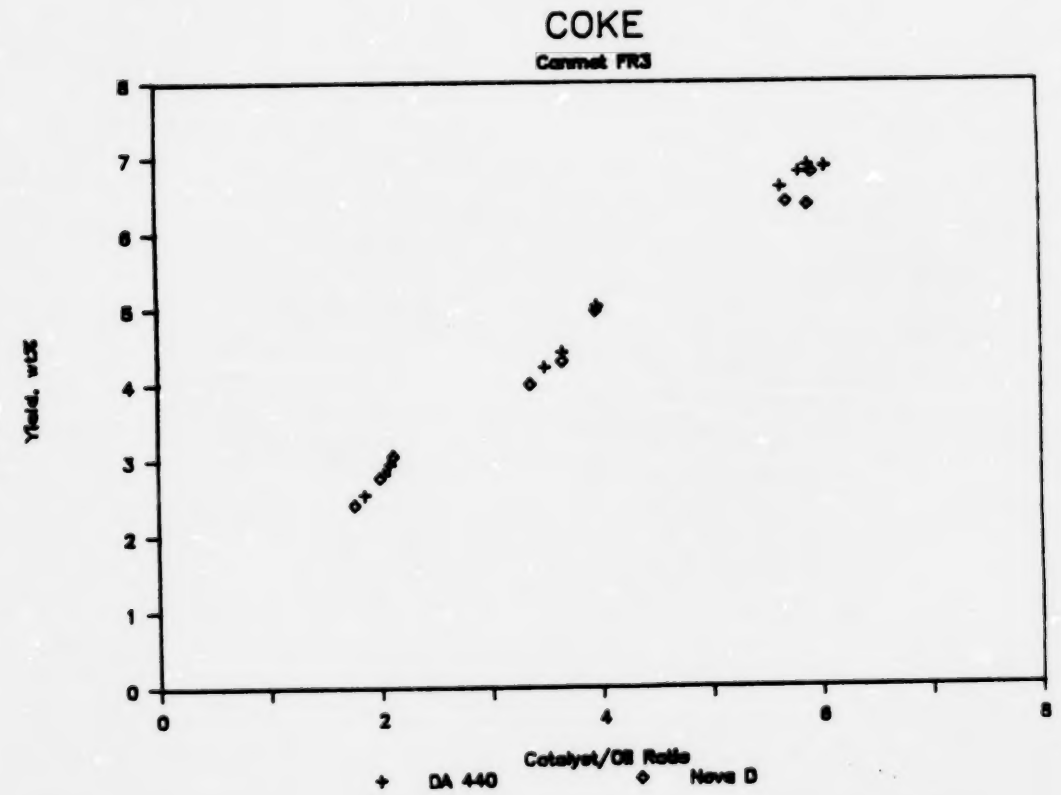

DECANT OIL
Canmet FR3
Yield, wt%
60
50
40
30
20
10
0
10
30
50
Conversion, wt%
490c
530c
DA 440
Nova D

Fig. 63


COKE
Canmet FR3
490C
510C
530C
Yield, wt%
Conversion, wt%
DA 440
Nova D


COKE
Canmet FR3
Yield, wt%
Catalyst/Oil Ratio
DA 440
Nova D

Comparison of Octane Enhancing and Metal Tolerant Catalyst

For conventional feedstocks, it is claimed that Octane Enhancing catalysts offer a number of benefits over conventional REY catalysts. Ritter et al. presented a comprehensive set of data on the effect of unit cell size on product yield and quality for:

(a) steam deactivated catalyst tested in fixed-fluid bed reactor (FFB)
(b) equilibirium catalyst tested in FFB reactor
(c) commercial unit data.

For testing equilibrium catalyst in a FFB, Ritter noted the following improvements with decrease in unit cell size:

(1) increase in C3 and C4 olefin make
(2) increase in gasoline yield and octane
(3) decrease in coke yield.

The feedstock used by Ritter et al was lighter than the IPL gas oil used in this contract but perhaps of similar quality.

		IPL VGO	Ritter's et al Feedstock (2)
	API Gravity	24.2	28.7
	Aniline Point	94	96
	UOP "K" Factor	12.0	11.9
Distillation	10%	369	375*
	50%	444	407
	90%	538	458

* (D1160 Distillation)

It is interesting to compare the yield variation presented by Ritter with IPL data at similar conversions.

Effect of Unit Cell Size on Product Distribution Comparison of Ritter's and Present Data

		Ritter A	MAT 136	Ritter D	MAT 139
H2	wt%	0.02	0.03	0.05	0.06
C1+C2	wt%	0.94	1.15	0.95	1.14
= C3	vol%	4.6	5.2	4.6	5.6
Total C3	vol%	5.9	6.9	5.9	7.1
C4=	vol%	3.1	4.7	3.6	5.4
Total C4	vol%	8.1	12.0	8.6	12.4
C5 Gasoline	vol%	54.1	58.5	54.6	57.4
LCO	vol%	26.6	19.2	26.6	19.0
DO	vol%	11.4	13.6	11.4	14.5
Coke	wt%	5.8	3.09	4.7	2.85
Conversion	vol%	62.0	67.2	62.0	66.6
Unit Cell A		24.44	24.42	24.29	24.28

The only area of agreement is the increase in light olefin with decrease in Unit cell size. Inspection of all the yield data at constant reactor temperature generated during the present contract shows that for equivalent conversion, the Nova D catalyst consistently produces more C3C4 olefin than the DA-440 catalyst for all feedstocks excepting the Shale Oil.

As discussed earlier with the IPL gas oil, the Nova D catalyst shows a marginally poorer gasoline selectivity when compared at equivalent conversion. This trend was also noted for the Coleville and Lloydminster gas oils and for the Suncor gas oil there was little differentiation between the two catalysts.

As discussed, decreased gasoline yield and increased light olefin yields are consistent with the reduced hydrogen transfer ability of the octane enhancing catalyst.

The large improvement in coke selectivity with decreasing unit cell size shown by Ritter is not shown by the present MAT data. Although the data presented above shows a marginal decline in selectivity with unit cell size, the coke selectivity plot for IPL gas oil (Fig.18) indicates that there is little differentiation between the two catalysts. Similar conclusions were reached for the Suncor, Coleville

and Lloydminster gas oils with the trends indicating some coke selectivity improvement with the DA-440 for the Coleville gas oil.

COKE FORMATION AND CATALYST DEACTIVATION

Improved coke selectivity is fundamental to improved catalyst performance. The coke selectivity plots presented in this report indicate that there is little difference in the selectivity of the two catalyst. These findings are apparently at variance with Ritter et al and also with Mott, who both present results showing improved coke selectivity for Octane enhancing catalyst.

The basic reason for the lack of improved coke selectivity of the Nova D catalyst is the lower activity of this catalyst for cracking non-conventional gas oils. A comparison of "catalytic" coke laydown at constant on-stream time shows that on average the Nova-D catalyst produces less coke on catalyst than the DA-440 catalyst. This is shown in Figs. 65-67 for the Coleville, Lloyd and Suncor gas oils. However, for these feedstocks the Nova D catalyst has to be operated at a higher C/O ratio than the DA 440 catalyst to achieve equal conversion thus mitigating the inherently lower coking tendency of the Nova D catalyst.

Voorhies relationship was used to determine if there were any further significant differences in the rate of coke formation between the two feedstocks. According to Voorhies, coke build-up on the catalyst is set by the on-stream time.

$$\text{Coke on Catalyst } (C) = A\, t^{n}$$

where t = catalyst on stream time and A and n are constants.

Thus: $\log C = \log A + n \log t$

Plots of Log C vs Log t for the six gas oils studied are shown in Figs. 64-69 and the values of n and A computed from these plots are given in Table 21.

With the exception of the IPL gas oil, the following trends are noted:

(1) The value of A is consistently less for the Nova D catalyst than the DA-440 catalyst
(2) The value of n is consistently greater for the Nova D catalyst.

A is the coke laydown after one second on-stream time, while n sets the rate of coke increase with time logarithmically.

The above observation would suggest that the Nova D catalyst may show lower coke makes than the DA-440 catalyst at the lower on-stream times. This may be significant for commercial riser cracking operation.

Coke is also directly related to temporary catalyst deactivation during the cracking cycle. Habib et al modified the coke classification proposed by Cimbalo et al as follows:

1. "Catalytic" coke, which is generated in association with acid-catalyzed cracking, increases exponentially with conversion, is lower with zeolite catalysts and is residence time-dependent. Catalyst coke, as a percent of feed, is usually directly proportional to the C/O ratio for the constant on-stream time.

2. "Contaminant" coke, which derives from catalytic dehydrogenation action of metals poisons such as nickel, vanadium, etc.

3. "Additive" coke which is that fraction of the coke which is independent of the C/O ratio or catalyst type, instead correlating with the basic nitrogen and average molecular weight of the feedstock as well as the Conradson Carbon Residue.

4. "Cat-to-oil" coke, which is a measure of unstripped but potentially strippable hydrocarbons; these are not really coke, but because of nonideal stripping in the commercial process, are also burned in the regenerator.

For the first four feedstocks studied during this contract, it is assumed that the major type of coke formation was catalytic coke. If coke is the major cause for catalyst deactivation, then there should be some correlation between catalyst deactivation rates and the Voorhies constants A and n. Fig.70 shows the relationship between the Voorhies gradient n (i.e. the rate of coke formation) and the decay constant Alpha. There is a general trend for increasing decay constant with decreasing gradient but no distinct relationship. Again Fig.71 shows that there is a general trend between an increase in the Voorhies "intercept" A (which is a measure of "initial" coke formation) and an increase in the catalyst decay constant. Qualitatively this would suggest that catalyst decay rates governed more by the

"initial" coke formation than the subsequent rate of coke formation. For interest, the catalyst decay rates are also compared to the basic nitrogen content and Conradson carbon.

Comparison of Average Catalyst Decay for DA-440 Catalyst with the Feedstock Basic Nitrogen and Conradson Carbon

	Decay Constant hr-1	Basic N ppm	Conradson Carbon wt%
Suncor	49.2	110	0.15
Coleville	48.2	100	0.06
Lloyd	63.4	250	0.13
IPL	77.7	310	0.43
Shale Oil	215.5	4570	0.18
CANMET	278.4	1876	0.08

As can be seen there is a definite trend for the various feedstocks between catalyst decay and basic nitrogen.

For the two low conversion gas oils, shale oil and CANMET oil, it must be assumed that additive coke is important both for coke formation and catalyst deactivation. In the case of the shale oil and CANMET gas oil, it is assumed that basic nitrogen components are responsible for the additive coke and the large catalyst decay constant.

For these two feedstocks the variation of the decay constant with Voorhies intercept and gradient show much more definite trends. There is a linear increase in the decay constant with:

(a) decreasing gradient (Fig.70)
(b) increasing intercept (Fig.71).

To summarize the above, it can be concluded that although there is a definite relationship between coke formation and catalyst deactivation, it is not a straight forward relationship especially for non-conventional feedstocks which may contain significant amounts of catalyst poisons.

Fig. 64

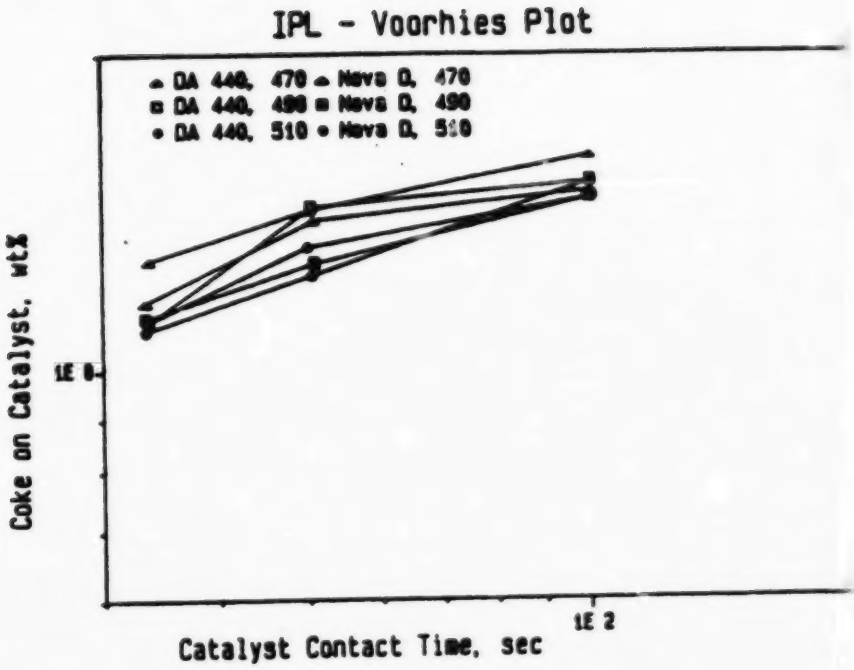

IPL - Voorhies Plot
▲ DA 440, 470 ▲ Nova D, 470
□ DA 440, 490 ■ Nova D, 490
• DA 440, 510 • Nova D, 510
Coke on Catalyst, wt%
1E 0
1E 2
Catalyst Contact Time, sec

Fig. 65

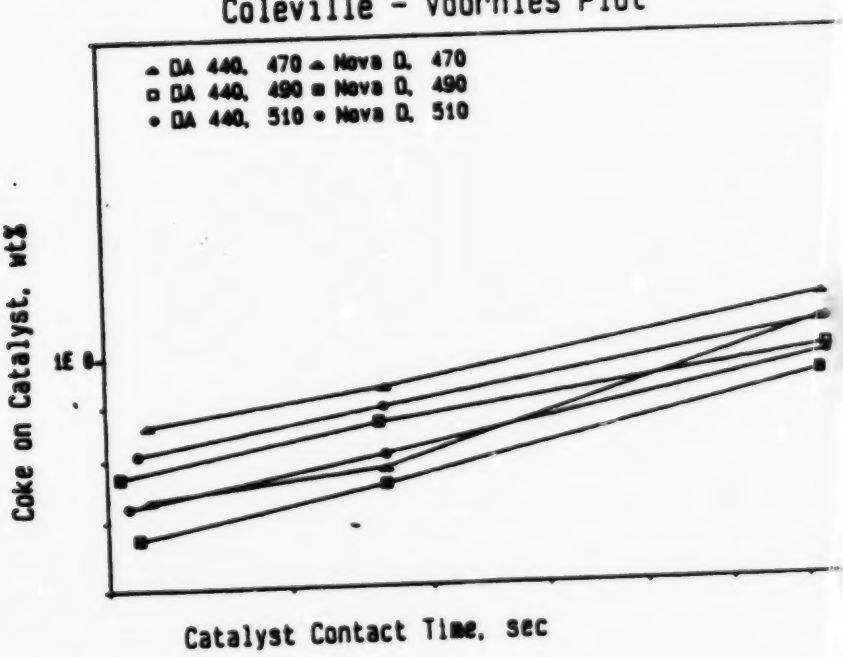

Coleville - Voorhies Plot
▲ DA 440, 470 ▲ Nova D, 470
□ DA 440, 490 ■ Nova D, 490
• DA 440, 510 • Nova D, 510
Coke on Catalyst, wt%
1E 0
Catalyst Contact Time, sec

Fig. 67

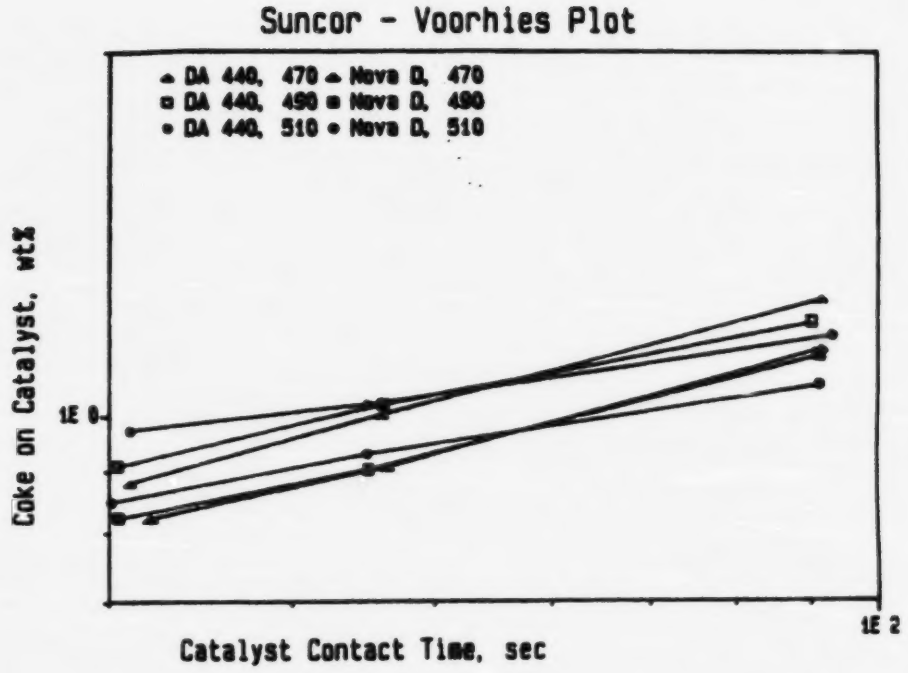

Suncor - Voorhies Plot
▲ DA 440, 470 ▲ Nova D, 470
□ DA 440, 490 ■ Nova D, 490
• DA 440, 510 • Nova D, 510
Coke on Catalyst, wt%
1E 0
1E 2
Catalyst Contact Time, sec

Fig. 66

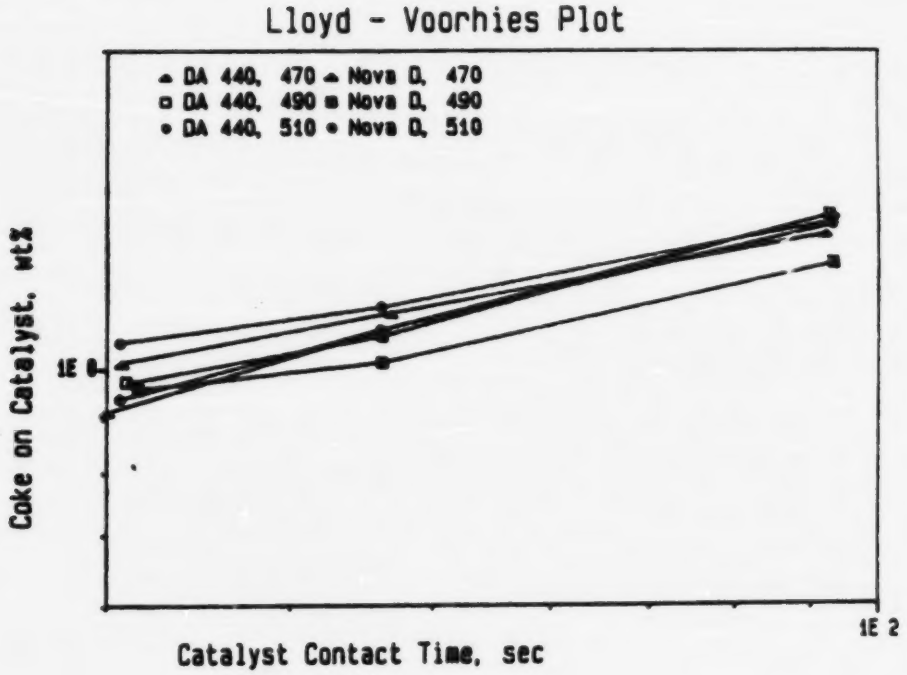

Lloyd - Voorhies Plot
▲ DA 440, 470 ▲ Nova D, 470
□ DA 440, 490 ■ Nova D, 490
• DA 440, 510 • Nova D, 510
Coke on Catalyst, wt%
1E 0
1E 2
Catalyst Contact Time, sec

Fig. 68

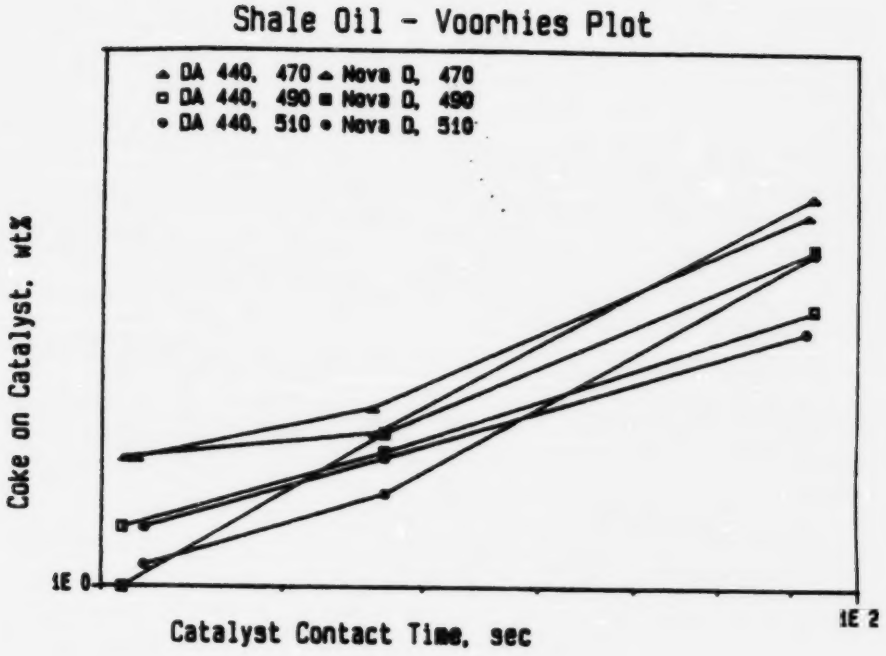

Shale Oil - Voorhies Plot
▲ DA 440, 470 ▲ Nova D, 470
□ DA 440, 490 ■ Nova D, 490
• DA 440, 510 • Nova D, 510
Coke on Catalyst, wt%
1E 0
1E 2
Catalyst Contact Time, sec

Fig. 69

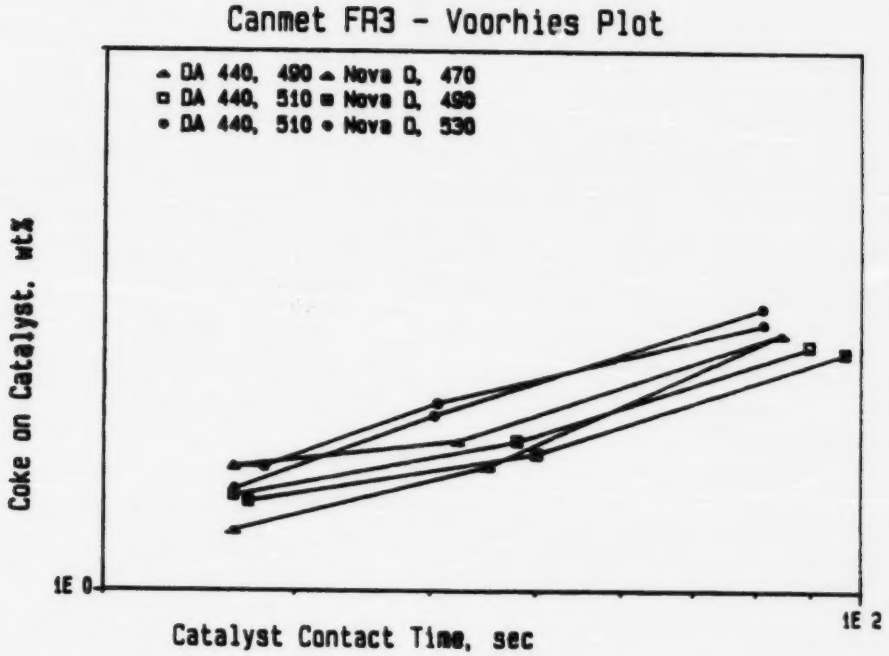

Canmet FR3 - Voorhies Plot
▲ DA 440, 490 ▲ Nova D, 470
□ DA 440, 510 ■ Nova D, 490
• DA 440, 510 • Nova D, 530
Coke on Catalyst, wt%
1E 0
1E 2
Catalyst Contact Time, sec

Fig. 70

Voorhies Constants vs Alpha

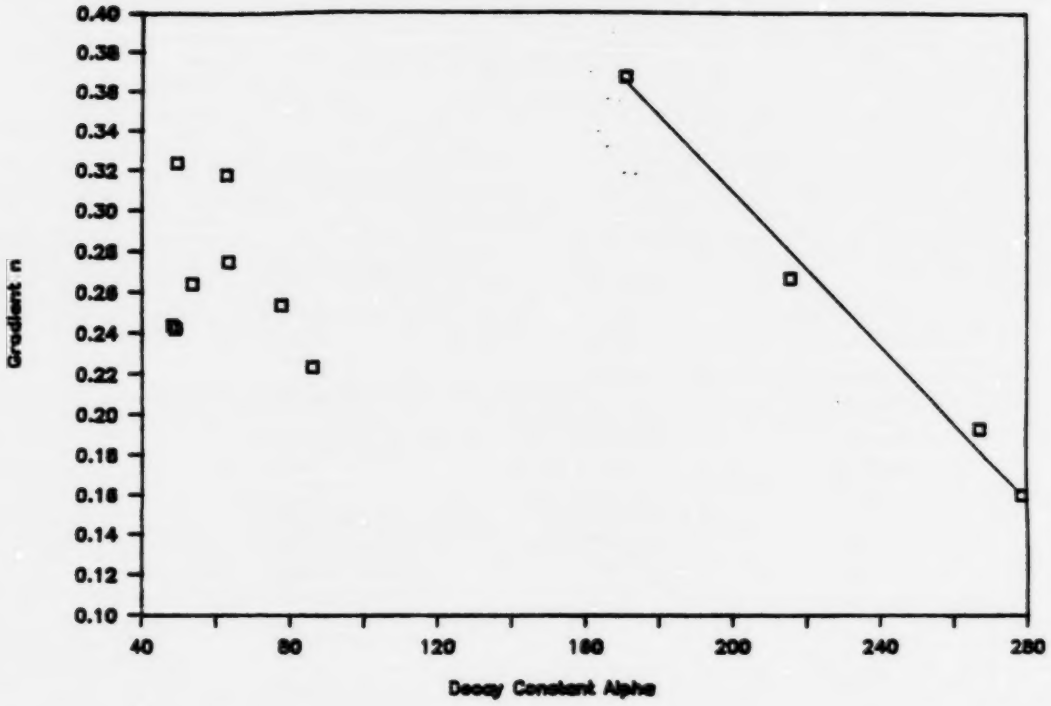


Fig. 71

Voorhies Constants vs Alpha

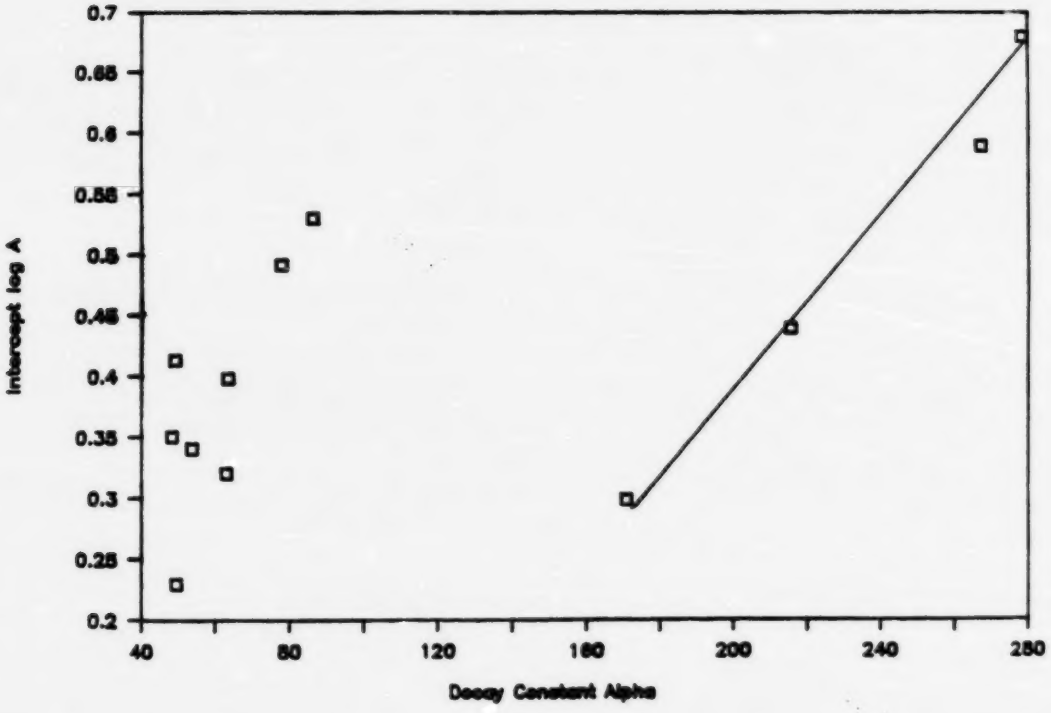


Table 21

Voorhies Coke Equation Constants log C = log A + n log t

	Feed Catalyst Temp C	Suncor DA 440	Suncor Nova B	Coleville DA 440	Coleville Nova D	Lloyd DA 440	Lloyd Nova D	IPL DA 440	IPL Nova D	Shale DA 440	Shale Nova D	Cansat FR3 DA 440	Cansat FR3 Nova D
Gradient n	470	0.3164	0.3069	0.2516	0.3650	0.2571	0.3718	0.2081	0.2084	0.3054	0.3261	0.1517	0.2181
	490	0.2456	0.2880	0.2317	0.3191	0.3334	0.2510	0.2592	0.2312	0.2567	0.3904	0.1576	0.1533
	510	0.1650	0.1980	0.2483	0.2876	0.2341	0.3303	0.2945	0.2309	0.2402	0.3866	0.1707	0.2083
Avg		0.2423	0.2643	0.2439	0.3239	0.2749	0.3177	0.2539	0.2235	0.2674	0.3677	0.1600	0.1932
Intercept log A	470	-0.5269	-0.5498	-0.4469	-0.6980	-0.3774	-0.5869	-0.2105	-0.2384	-0.3949	-0.4314	-0.1533	-0.2821
	490	-0.4032	-0.5170	-0.4552	-0.6542	-0.5160	-0.4015	-0.3266	-0.2966	-0.3511	-0.5819	-0.1746	-0.1755
	510	-0.2612	-0.3616	-0.4635	-0.5736	-0.3265	-0.5154	-0.4113	-0.2947	-0.3291	-0.5791	-0.1752	-0.2386
10^A	470	0.2972	0.2820	0.3574	0.2004	0.4194	0.2589	0.6159	0.5776	0.4028	0.3703	0.7026	0.5223
	490	0.3952	0.3041	0.3506	0.2217	0.3048	0.3967	0.4714	0.5051	0.4456	0.2619	0.6690	0.6676
	510	0.5480	0.4349	0.3440	0.2669	0.4715	0.3052	0.3879	0.5073	0.4687	0.2636	0.6680	0.5773
Avg		0.4135	0.3403	0.3506	0.2297	0.3986	0.3203	0.4917	0.5300	0.4390	0.2986	0.6799	0.5890
Alpha hr-1	470	45.9	57.1	53.5	52.7	65.5	60.2	87.0	104.9	273.1	194.2	293.9	319.6
	490	51.8	52.8	48.3	48.7	62.0	63.0	71.8	78.9	195.6	173.9	304.6	257.2
	510	49.9	51.5	42.8	47.5	62.8	65.4	74.4	75.0	177.8	144.2	236.7	224.5
Avg		49.2	53.8	48.2	49.6	63.4	62.9	77.7	86.3	215.5	170.8	278.4	267.1

CONCLUSIONS

(1) The conventional gas oil (IPL VGO) showed higher conversions and gasoline yields than any of the non-conventional gas oils.

(2) Three of the non-conventional gas oils, Coleville, Suncor, and Lloyd, are acceptable FCC feedstocks. The lower conversions and gasoline yields for these gas oils are directly correlatable with their hydrocarbon compositions.

(3) The much lower conversions obtained for the shale oil were attributed to the catalyst being poisoned by basic nitrogen compounds. The shale oil is not an acceptable FCC feedstock for this reason. Once the effect of the basic nitrogen has been mitigated, then based on the hydrocarbon composition, the shale oil would be equivalent to IPL gas oil as a FCC feedstock.

(4) The CANMET gas oil gave marginally better conversion and gasoline yield than the shale oil. This is somewhat surprising considering the much poorer quality of the CANMET gas oil. The low conversion and gasoline yield is attributed to the lack of crackable components in the gas oil combined with catalyst poisoning effects.

(5) Over the range of severities studied, there was gasoline over cracking for the conventional crude but little if any gasoline overcracking for the non-conventional crudes.

(6) Kinetic studies showed that the non-conventional gas oils showed lower cracking rates than the conventional gas oil and thus may benefit from more active catalyst. This difference is attributed to the relatively greater concentration of Naphthenic components in the crackable fraction of non-conventional gas oils.

(7) The Nova D (octane enhancing) catalyst was marginally more active cracking the conventional gas oil than the DA-440 (metals tolerant) catalyst. This is in agreement with the microactivity data. However, for all the non-conventional gas oils, the DA-440 catalyst showed the greater activity (highest conversion).

(8) The selectivity of the two catalysts were closely similar. Where there were differences, DA-440 was more

selective for gasoline production while Nova D was more selective for C3C4 production. In the C3C4 fraction at equivalent conversion the Nova D catalyst produced a greater percentage of olefin than the DA-440 catalyst as would be expected from the octane enhancing catalyst. In addition, Nova D produced more hydrogen than DA-440.

(9) There was no measurable difference in the coke selectivity of the two catalyst under MAT conditions. This was attributed to the lower activity of the Nova D catalyst requiring a greater C/O for equivalent conversion. Since Nova D produces lower catalytic coke on catalyst than DA-440.

(10) Operating the MAT unit at the experiemental conditions used in this study gave useful consistent data suitable for input into a kinetic model.

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APPENDIX 1

Kinetic Model

FCCU OPERATIONS

REACTOR KINETIC MODELLING

A.E. POPE

MARCH, 1987

FILE NO. 140-86-15

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KINETIC MODELLING OF FCCU REACTOR OPERATIONS

1. INTRODUCTION

Application of a kinetic model to the data generated during a microactivity test serves a twofold purpose. First, the effects of reactor configuration may be eliminated so that the derived kinetic parameters are transferable between different reactor configurations, for example, from a fixed bed reactor to a riser transfer line. Second, the kinetic parameters from the model are related directly to the basic reactions occurring during cracking thus allowing straightforward comparison of the relative rates of reaction for different catalyst-feed combinations.

Although Blanding(1) developed a model using a simple rate expression, early models for conversion (eg Voorhies(2) and Andrews(3)) were empirical or semi-empirical. The first comprehensive model applicable to a variety of reactor configurations and based on the kinetics of gas oil cracking, gasoline formation, and with account taken of catalyst deactivation, was developed by Weekman and Nace at Mobil R&D(6). This model was used to investigate the effects of different charge stock components on cracking kinetics(7) and to correlate these effects(8). Ultimately, the Mobil group devised a much more complex kinetic model requiring specialized analysis of the charge stock, but capable of predicting conversion, gasoline, light fuel oil and light ends yields(9).

Meanwhile, in Canada, Wojciechowski and his co-workers at Queen's University, Kingston developed a more general formulation of Weekman and Nace's original simple mechanism describing gas oil cracking to gasoline and gas-coke products(10,11). By introducing a feed dependent 'refractoriness parameter' superimposed on first order cracking kinetics, Wojciechowski and his colleagues effectively derestricted the overall order of cracking from the fixed second order kinetics assumed in the Weekman and Nace model. Wojciechowski's group also allowed the catalyst deactivation to be represented by a variable mth order decay function rather than the fixed first order function used in the Mobil model.

Other models following Weekman and Nace's concept have found commercial application. Paraskos et al(12,13), at Gulf R&D, extended the Weekman and Nace model to simulate cracking in a commercial transfer line reactor under both isothermal and adiabatic conditions. At about the same time, a group at Amoco set up correlations, using pilot plant data, to establish a comprehensive FCCU design model(14). Although not immediately apparent, it is possible to derive the general form of equations used in the Amoco correlations from the formulation presented by Weekman and Nace.

Since most of the FCCU kinetic models referenced in the literature are variants or extensions of the Weekman and Nace model, this is an obvious starting point in selecting a model suitable for correlating microactivity test data. In addition to being the genesis of current kinetic models, the Mobil model offers other advantages. The original concept of the model was to provide a vehicle for transposing data from fixed bed laboratory reactors to commercial cracking applications. Also, the formulation was kept relatively simple. Only an overall cracking rate constant and a catalyst activity decay constant are required to define conversion; a second pair of rate constants define the gasoline selectivity. This last point is an important consideration if the available number of microactivity test runs at any particular condition is limited. Should more run data eventually become available, it is quite feasible to move from Weekman and Nace's original model to one of the more advanced versions, such as that of the Wojciechowski school, where the additional data can be used to provide more information and insight into the effectiveness of feed-catalyst combinations.

2. MODEL FORMULATION

The description of the model is based on the detailed presentations given by Weekman and Nace in the series of papers quoted as references 4-6.

2.1 Reactor Equation

Since steady state conditions cannot be assumed a priori for some reactor configurations, notably fixed beds, the starting point is the general 1-D reactor continuity equation for plug flow(15),

$$\frac{\delta y}{\delta t} + U \cdot \frac{\delta y}{\delta x} = R(y) \qquad (1)$$

y is the mole fraction of the particular species, U is the linear velocity through the reactor, R(y) is the mole fraction rate of formation of species y, while t and x are the temporal and spatial coordinates respectively. A more convenient formulation is in terms of dimensionless coordinates. With a total reaction time of tc - variously referred to as the 'process time' or 'time on stream' - and for a reactor (ie catalyst) total length L, the dimensionless coordinates θ and z may be defined as

$$\theta = t / tc \qquad \text{and} \qquad z = x / L \qquad (2)$$

so that the continuity equation becomes,

$$\frac{1}{tc} \cdot \frac{\delta y}{\delta \theta} + \frac{U}{L} \cdot \frac{\delta y}{\delta z} = R(y) \qquad (3)$$

The linear velocity is defined by the mass feed rate to the reactor, F, the reacting vapour density, ρ_v, the reactor cross-sectional area, A, and the voidage fraction of the catalyst, ϵ, as

$$U = \epsilon F / \rho_v A \qquad (4)$$

Substituting this in the continuity equation, with reactor volume V defined as L·A, gives

$$\frac{tv}{tc} \cdot \frac{\delta y}{\delta \theta} + \frac{\delta y}{\delta z} = \frac{\epsilon \sigma_v V}{F} R(y) \qquad (5)$$

where tv, the vapour contact time, or reciprocal vapour space velocity, is given by

$$tv = \epsilon \sigma_v V / F \qquad (6)$$

The liquid volumetric space velocity is conventionally defined as,

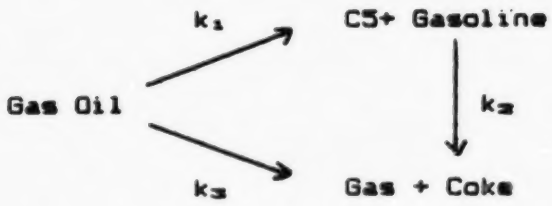
$$S = F / \sigma_l V \qquad (7)$$

with σ_l the feed liquid density at ambient conditions. Using this to substitute for V/F, the final form for the general continuity equation for a catalytic reactor is,

$$\frac{tv}{tc} \cdot \frac{\delta y}{\delta \theta} + \frac{\delta y}{\delta z} = \epsilon \frac{\sigma_v}{\sigma_l} \frac{1}{S} R(y) \qquad (8)$$

2.2 Conversion and Selectivity Kinetics

The following simplified scheme was proposed by Weekman and Nace(6) represent the kinetics involved in gas oil cracking.



(9)

Thomas and Thomas(15) provide a good description of the selectiv characteristics in such reaction schemes involving both parallel consecutive reactions.

Assuming that the overall cracking rate for gas oil is second order that gasoline cracking is first order, the rates of formation of oil $R(y_1)$ and gasoline $R(y_2)$ are, respectively

$$R(y_1) = -(k_1 + k_3) \cdot y_1^2 \, \emptyset \qquad (10)$$

$$R(y_2) = k_1 y_1^2 \, \emptyset - k_2 y_2 \, \emptyset \qquad (11)$$

where y_1 and y_2 are the instantaneous mole fractions of gas oil and gasoline, k are the rate constants (mole fraction / unit time) and represents the instantaneous fractional catalyst activity. It assumed that gas oil cracking and gasoline cracking involve the s catalyst sites so that a common activity decay term applies to b reactions.

If the fractional catalyst activity is unity at time zero on fr catalyst but decays as a first order function during reaction then rate of decay of activity is,

$$\frac{d\emptyset}{dt} = -\alpha\emptyset \qquad (12)$$

where α is the decay rate constant. Integrating to time t, with $\emptyset$ = when t = 0, gives the instantaneous fractional activity at time t as

$$\emptyset = e^{-\alpha t} \qquad (13)$$

In terms of the dimensionless time θ, equation 2

$$\phi = e^{-\mu\theta} \qquad (14)$$

with the dimensionless group

$$\mu = \alpha tc \qquad (15)$$

Substituting for ϕ and the rates R in the 1-D reactor continuity equation 8, gives two partial differential equations describing the mole fractions of gas oil and gasoline in a catalytic reactor.

$$\beta \frac{\delta y_1}{\delta \theta} + \frac{\delta y_1}{\delta z} = -\epsilon \frac{\sigma_v}{\sigma_1} \frac{1}{S} k_o y_1^2 e^{-\mu\theta} \qquad (16)$$

$$\beta \frac{\delta y_2}{\delta \theta} + \frac{\delta y_2}{\delta z} = \epsilon \frac{\sigma_v}{\sigma_1} \frac{1}{S} (k_1 y_1^2 - k_2 y_2).e^{-\mu\theta} \qquad (17)$$

where $\beta = tv/tc$, and $k_o = k_1 + k_2$.

For a reactor such as a co-current flow riser line, or a moving bed, where steady state conditions pertain, the composition depends only on the distance along the reactor. The composition at any given point is time invariant and the derivative in θ in the continuity equation is zero. For a fixed bed reactor, the composition at any point along the bed will change with time as the catalyst is deactivated. However, if the contact time of the vapour in the reactor is much shorter than the total time on stream for the catalyst, then $tv \ll tc$ and $\beta \approx 0$, so the time derivative term becomes negligble. In this case the continuity equations for gas oil and gasoline reduce to two ordinary differential equations,

$$\frac{dy_1}{dz} = -\frac{K_o}{S} y_1^2 e^{-\mu\theta} \qquad (18)$$

and

$$\frac{dy_2}{dz} = \frac{(K_1 y_1^2 - K_2 y_2)}{S} e^{-\mu\theta} \qquad (19)$$

For simplicity the system dependent density terms and catalyst voidage fraction have been incorporated into the rate constant terms in these equations ie

$$K = \epsilon \frac{\rho_v}{\rho_a} k \qquad (20)$$

In physical terms, the assumption in applying these equations to a fixed bed reactor is that the vapour residence time is sufficiently short in comparison to the activity decay rate that the vapour sees only catalyst of essentially constant age during its traverse through the reactor. Typically, in a microactivity test, tc will be about 60 sec while tv will be the order of 0.5 to 1 sec, so $\beta \approx 0.01$. The half-life of the catalyst activity is usually in the range of 25 to 50 sec, and neglect of the time derivative terms in the continuity equation is justified.

2.3 Fixed Bed Reactor

2.3.1 Conversion and Average Conversion

The ordinary differential equation 18 may be solved for y_1, the gas oil mole fraction, given the initial condition, $y_1(0,\theta) = 1$, $z = 0$, for all θ,

$$y_1(z,\theta) = \left(1 + \frac{K_o}{S} z e^{-\mu\theta} \right)^{-1} \qquad (21)$$

Usually with a fixed bed reactor, sample is collected at the outlet of the reactor ($z = 1$) over the time period $\theta = 0$ to $\theta = 1$, so that the ultimate concentration of gas oil in the sample is the time-averaged value of the instantaneous gas oil concentrations at the reactor exit.

$$\overline{y_1} = \int_0^1 y_1(1,\theta)\, d\theta \qquad (22)$$

The time-averaged conversion, $\bar{f}$ is,

$$\bar{f} = 1 - \overline{y_1} \qquad (23)$$

Performing the integration in equation 22, the overall conversion is,

$$\bar{f} = \frac{1}{\alpha t_c} \log_e \left[\frac{1 + X}{1 + X e^{-\alpha t_c}} \right] \qquad (24)$$

where $X = K_o/S$.

Equation 24 relates the time-averaged conversion to the space velocity and time-on-stream. The equation may be made explicit in the catalyst/oil ratio by noting that

$$C/O = 1 / S t_c \qquad (25)$$

which may be used to replace t_c in equation 24.

2.3.2 Gasoline Yield and Average Gasoline Yield

The instantaneous gasoline yield is y_2, the solution of equation 19. A closed form analytical solution of equation 19 is not available although a somewhat complex solution was given by Weekman and Nace for the ratio of equations 18 and 19. An alternative approach is to solve 19 numerically from z = 0 to z = 1, given that $y_2(0,\theta) = 0$ when z = 0, for specific values of time, θ. The instantaneous gas oil mole fraction, y_1, required to solve equation 19 is given by equation 21.

Solution of equation 19 at z = 1 gives the instantaneous gasoline yield at the reactor exit corresponding to time θ, ie $y_2(1,\theta)$. Solving the equation at increments of θ in the range 0 to 1 allows the time-averaged gasoline yield to be calculated as

$$\overline{y_2} = \int_0^1 y_2(1,\theta)\, d\theta \qquad (26)$$

with the integral determined numerically using, for instance, Simpson's rule.

3. RATE CONSTANT DETERMINATION

The rate equations and solutions developed in the last section give the conversion and gasoline yield as functions of the space velocity and time-on-stream, and in terms of four rate constants,

$$\bar{f} = f(S,tc\ ;\ K_o,\alpha) \qquad (27)$$

and

$$\bar{\bar{y}}_2 = f(S,tc\ ;\ K_1,K_2) \qquad (28)$$

By fitting these functions to the measured conversions and gasoline yields from microactivity tests for a particular feed-catalyst combination , with the space velocity and time-on-stream taken as the independent variables, the rate constants can be determined using standard nonlinear regression techniques. For the overall gas oil cracking rate constant K_o and the activity decay rate constant α, the experimental data are regressed using equation 24 to calculate the response function - conversion. In the case of the gasoline rate constants K_1 and K_2, calculation of the response function during regression analysis involves the numerical solution of the differential equation 19 at a series of time increments followed by numerical integration to obtain the time-averaged gasoline yield.

To carry out the regressions a multiple nonlinear regression program based on Marquardt's algorithm(16), which utilized user-supplied nonlinear response functions, was employed. Two separate functions to calculate either the conversion or the gasoline yield were written for use with the regression program.

The function for the conversion consisted simply of computing equation 24. The second function, for the gasoline yield, involved solution of equations 21 and 19 utilizing an explicit fourth order Runge-Kutta-Fehlberg technique(17) with imbedded error estimation for automatic step control(18), followed by quadrature with Simpson's rule.

The two regression programs were run in sequence, first to determine K_o and α from the conversion fit, then to calculate K_1 and K_2 by fitting the gasoline yield data.

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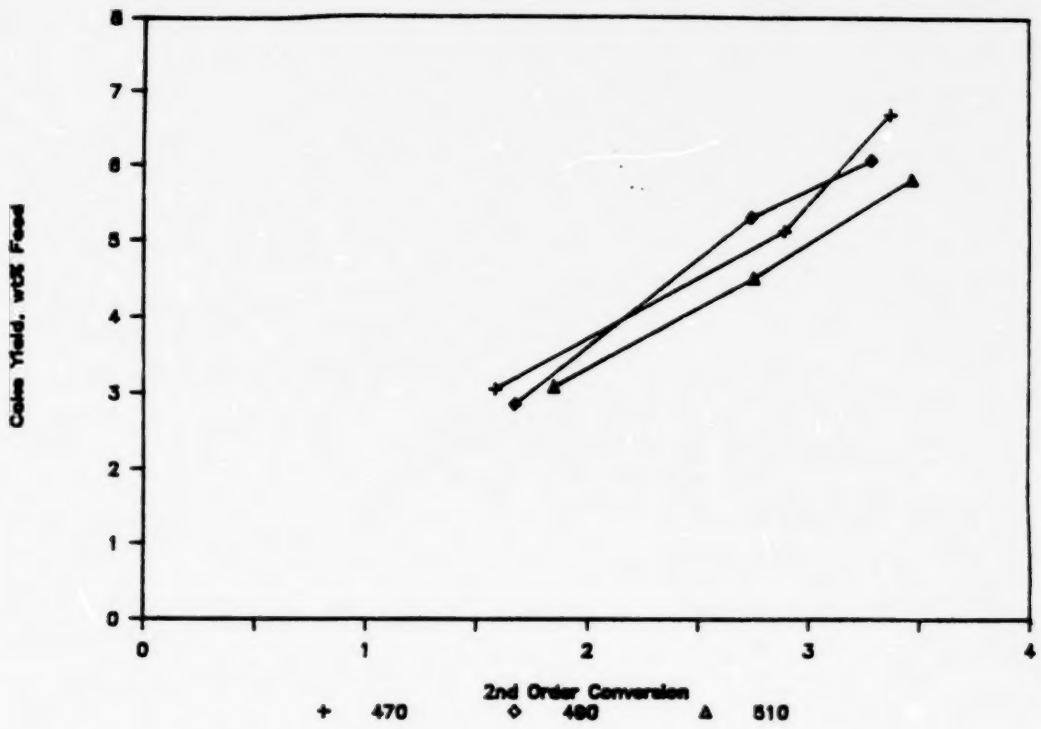
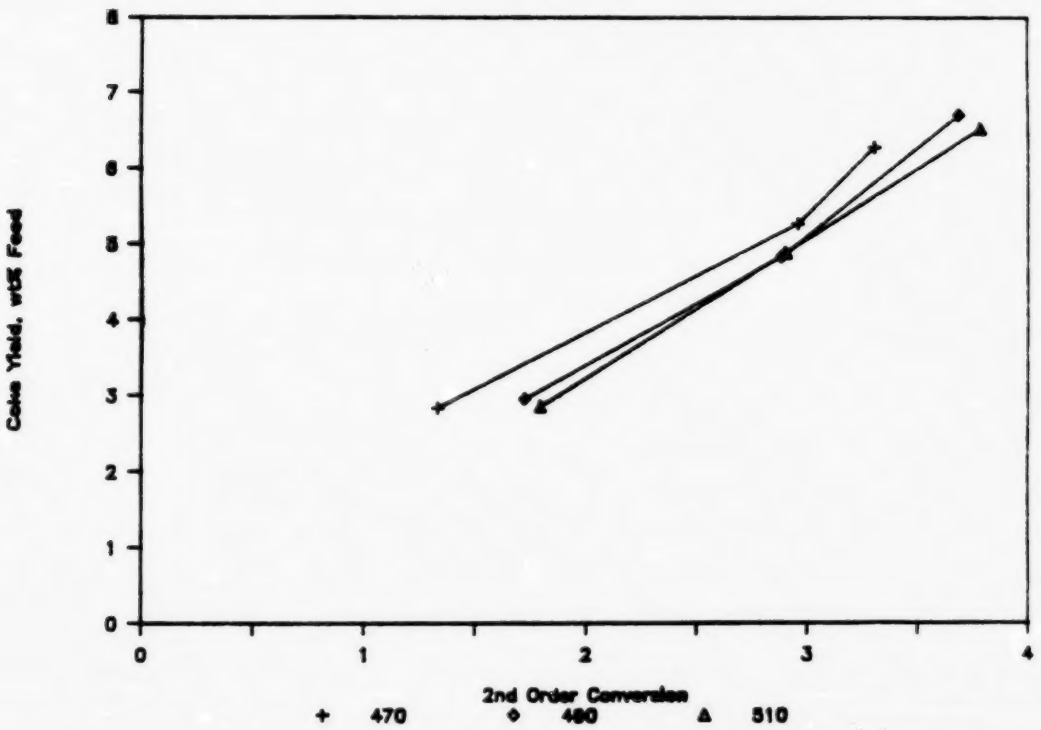
APPENDIX 2

Additional Tables and Graphs

IPL & DA 440



IPL & Nova D



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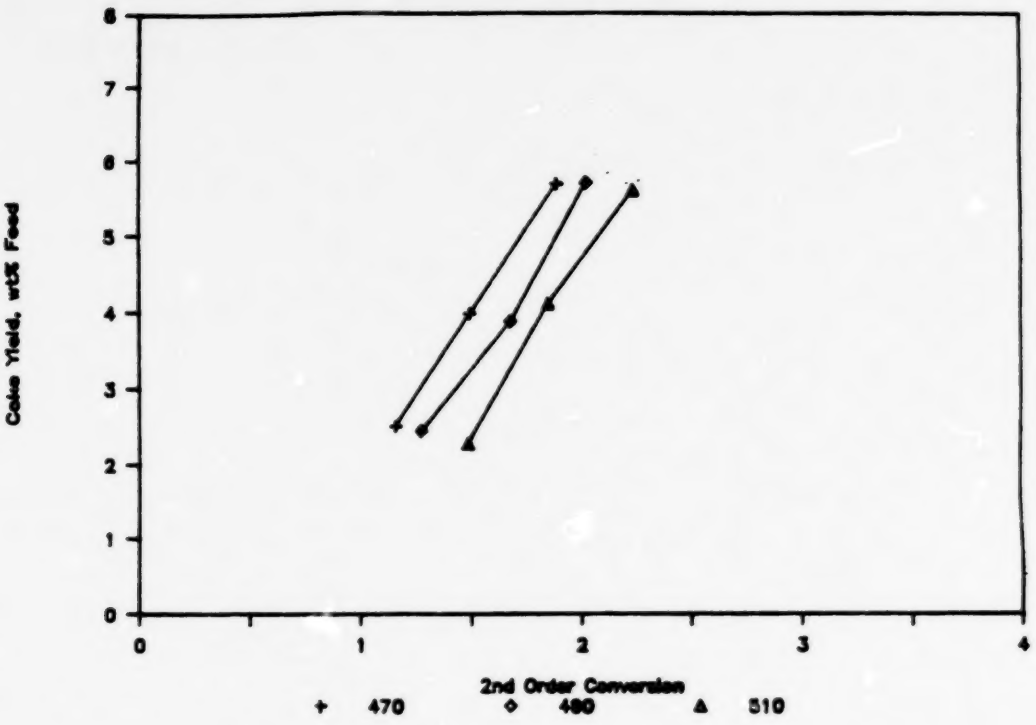
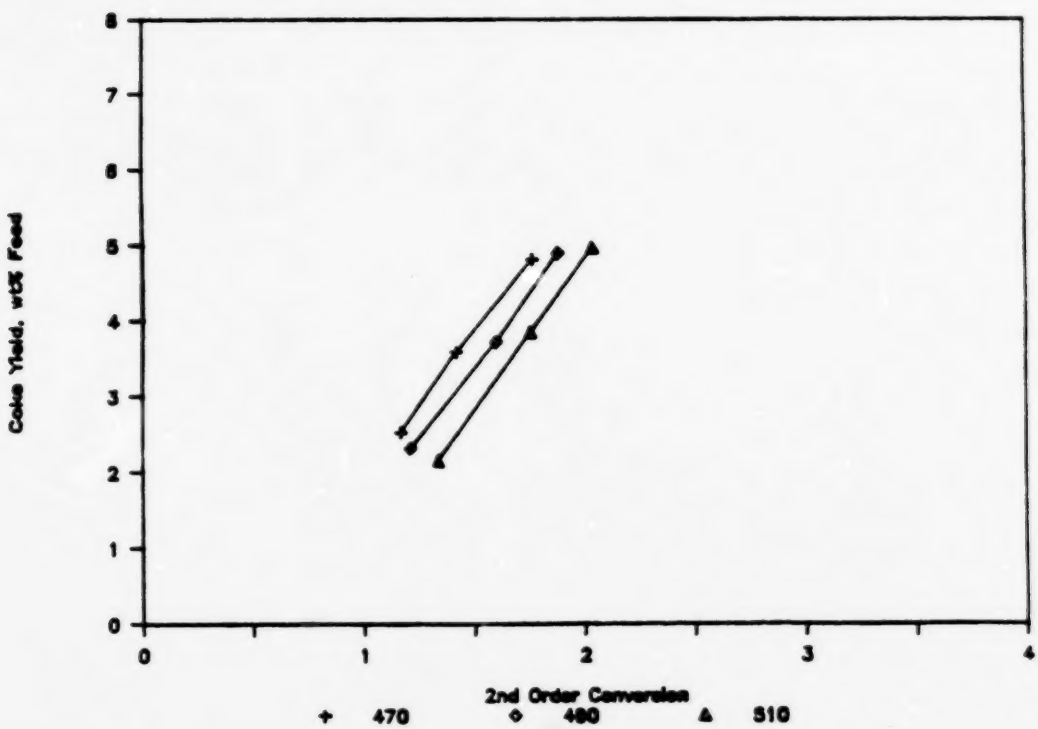
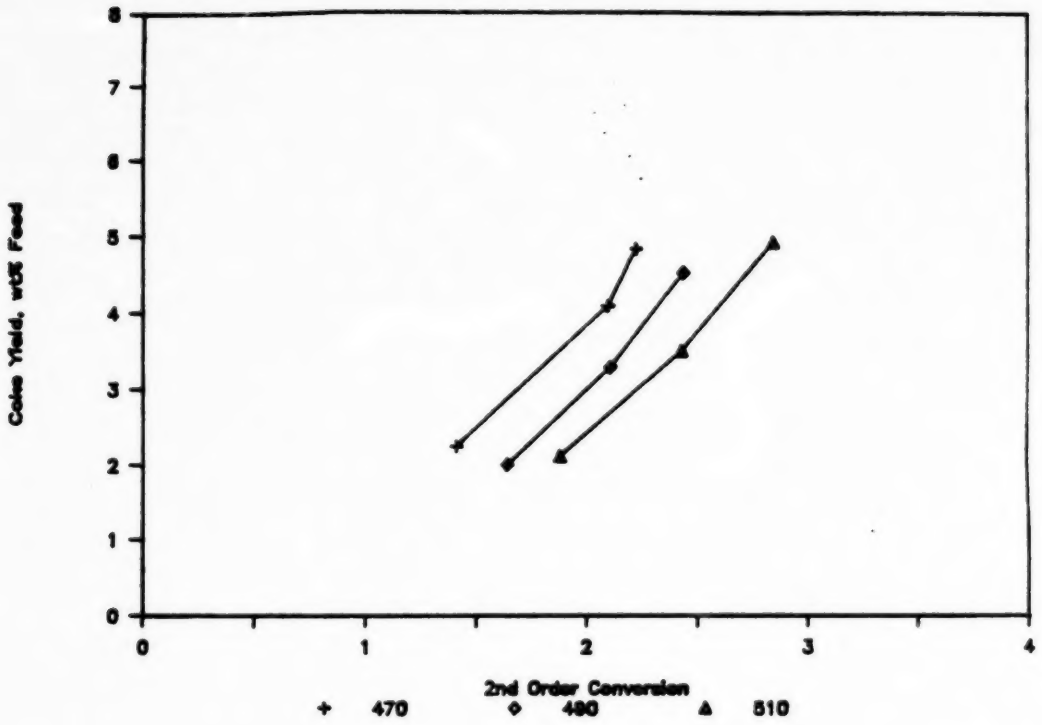


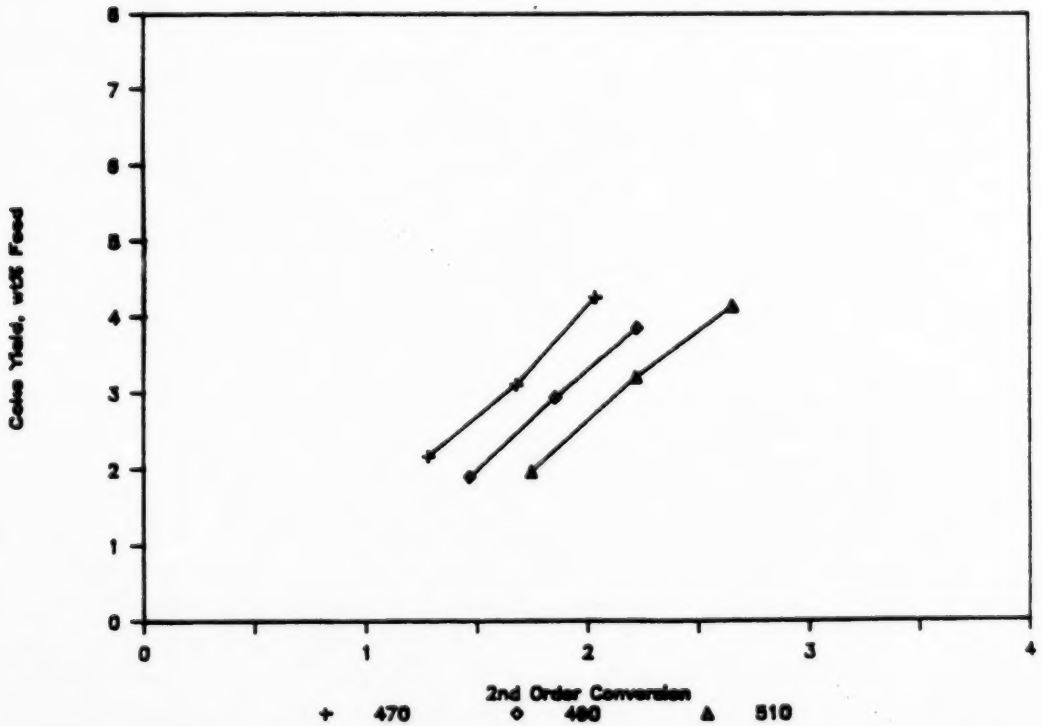
Suncor & Nova D



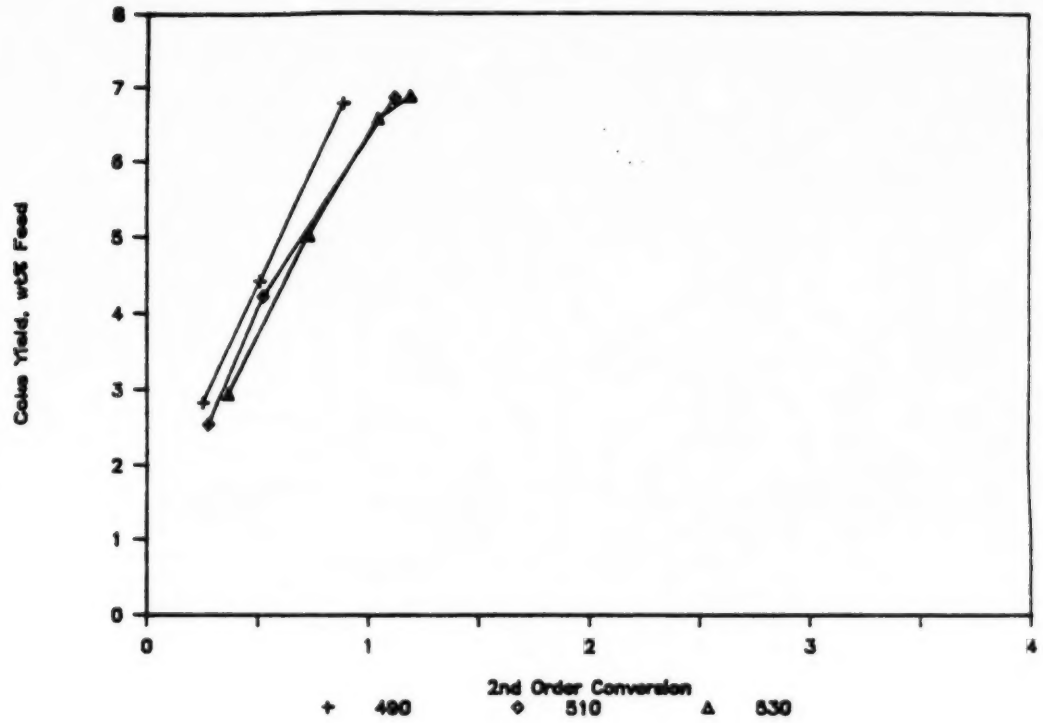
Coleville & DA 440



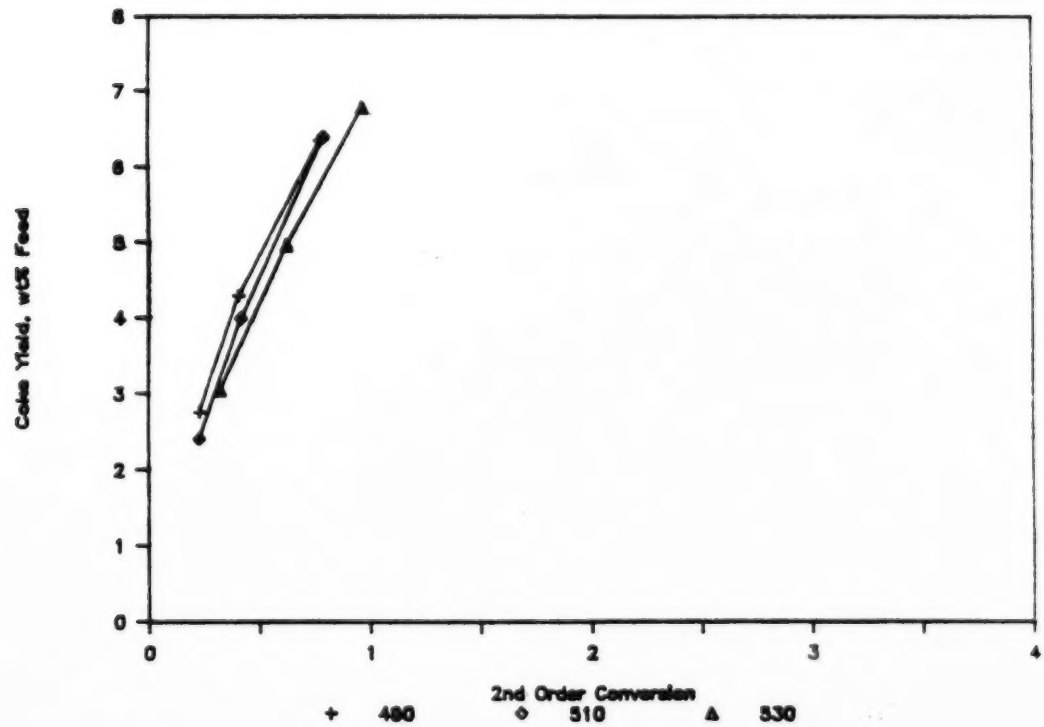
Coleville & Nova D



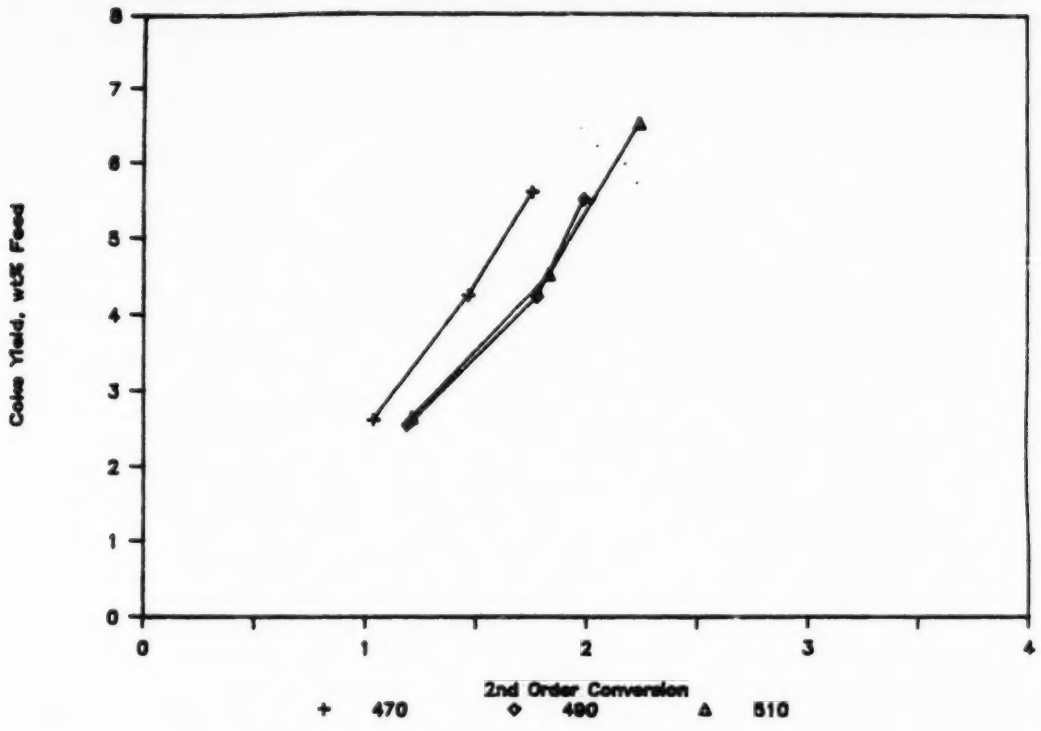
Canmet FR3 & DA 440



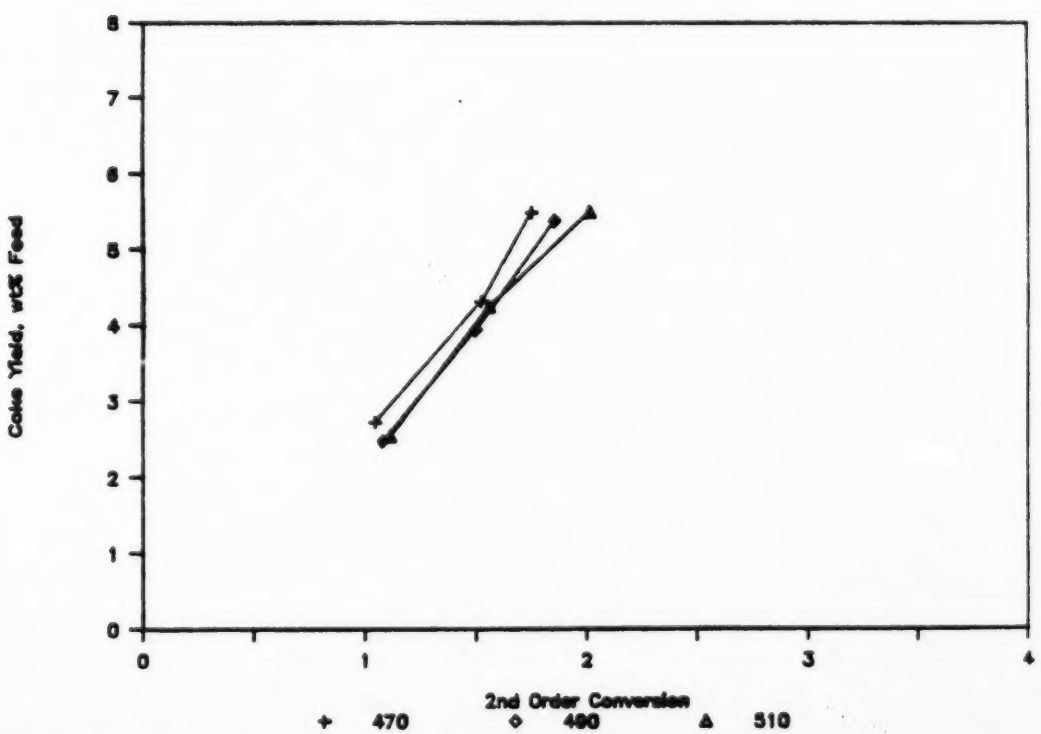
Canmet FR3 & Nova D

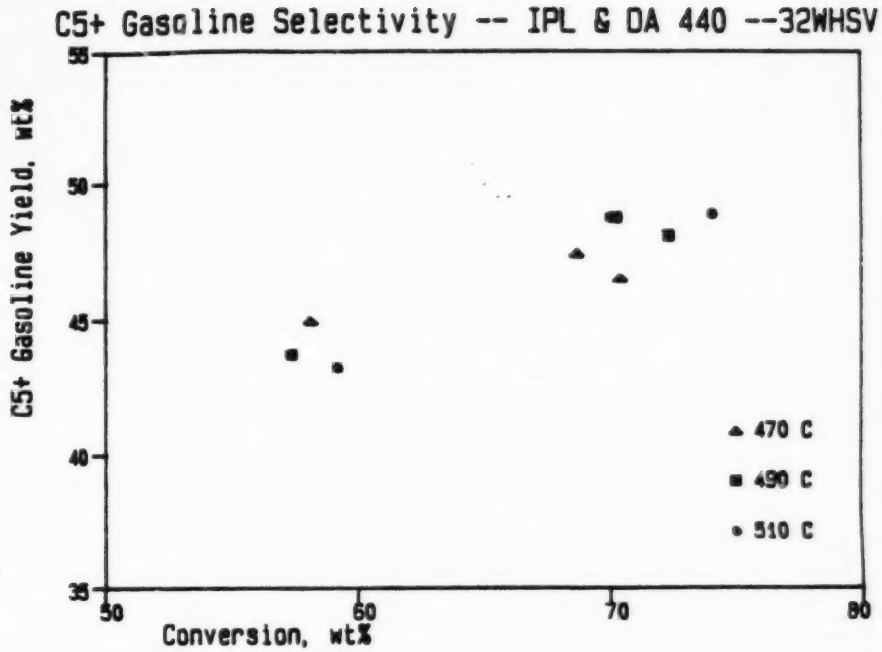


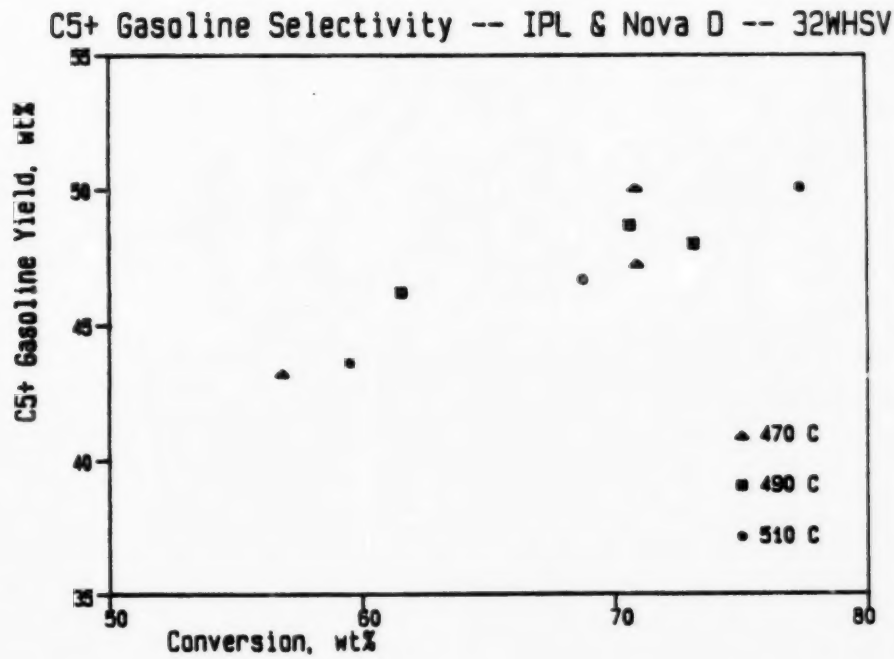
Lloyd & DA 440

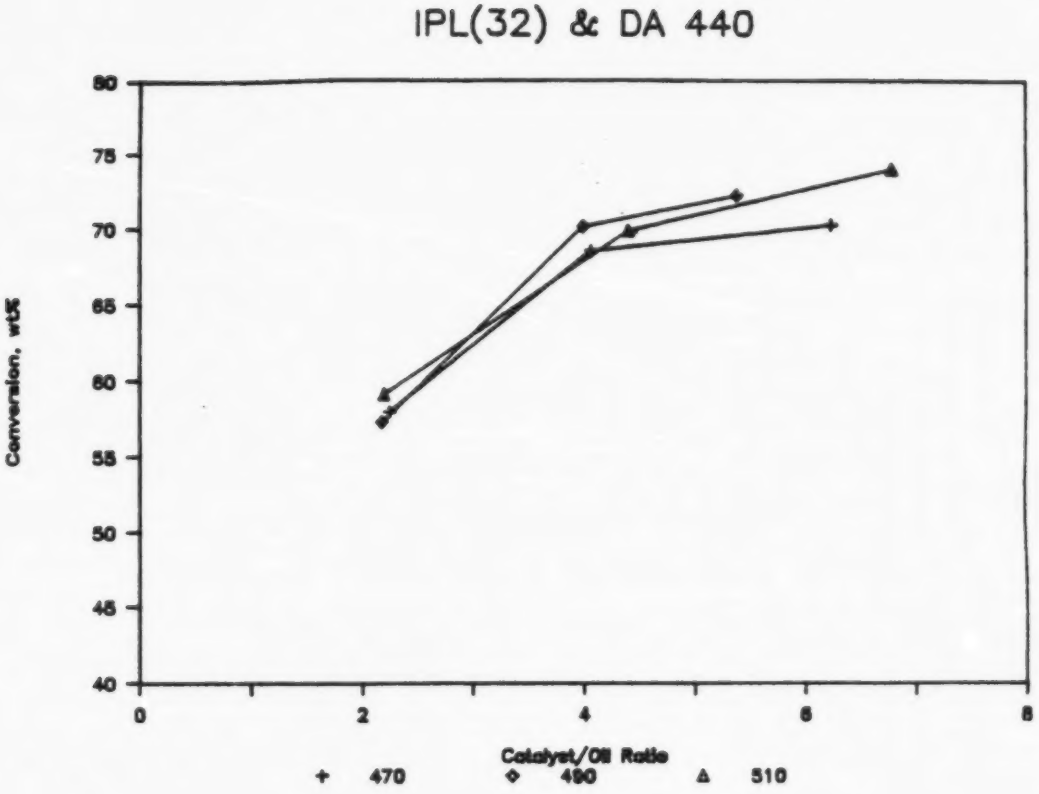


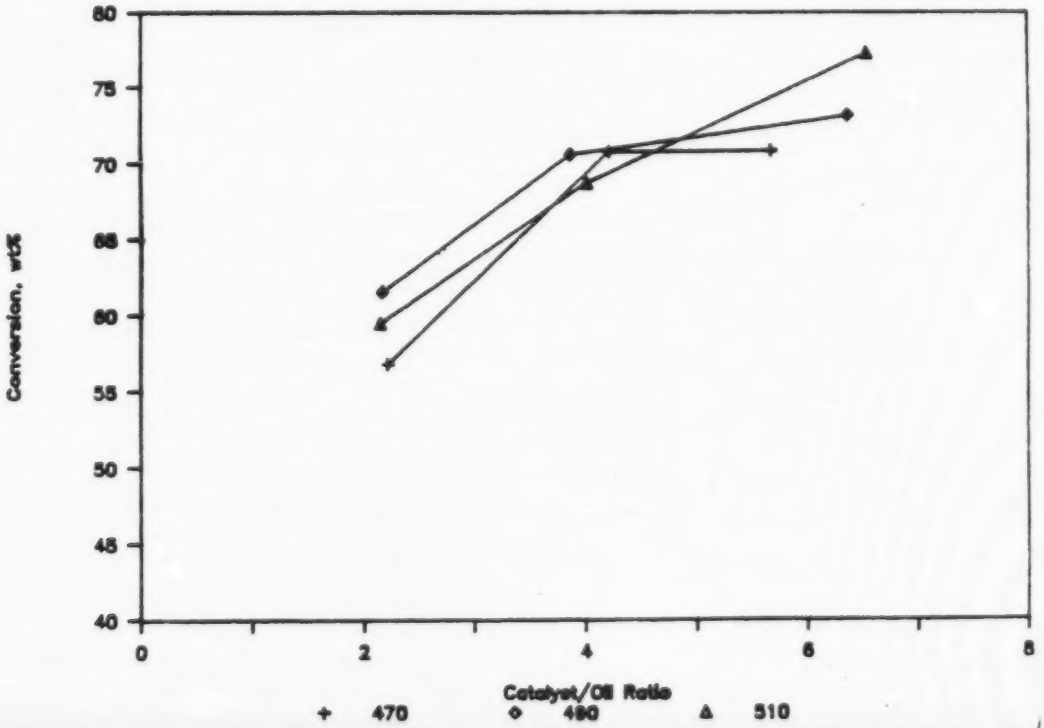
Lloyd & Nova D

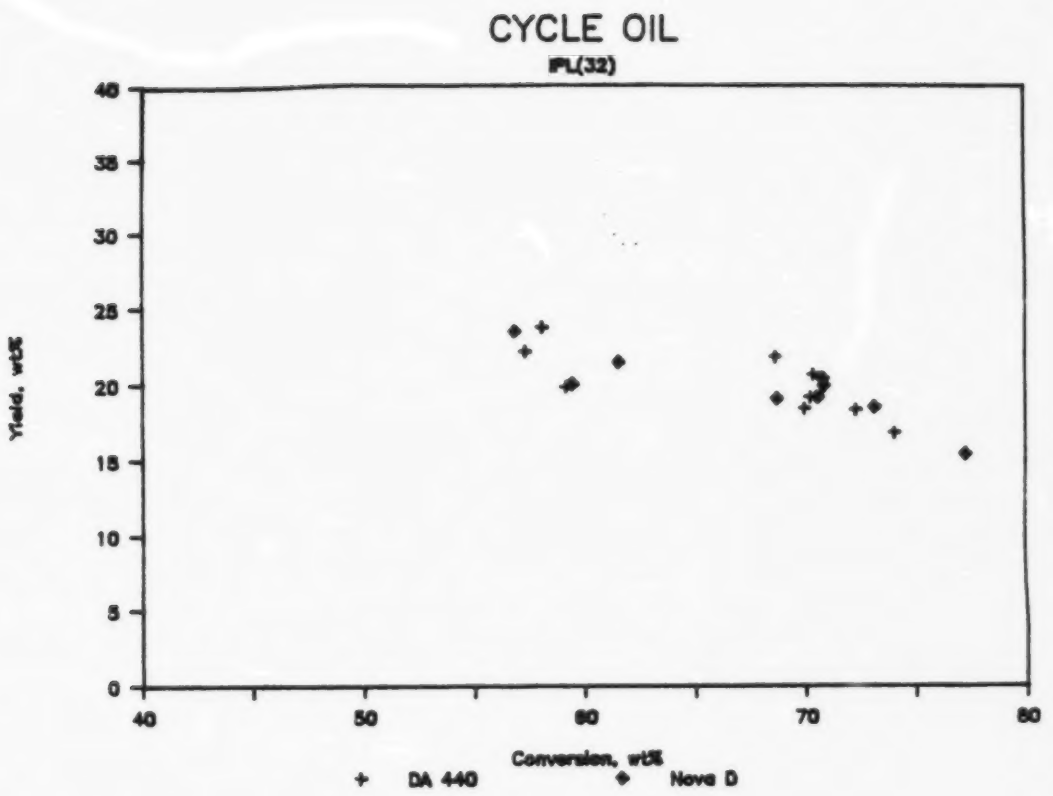


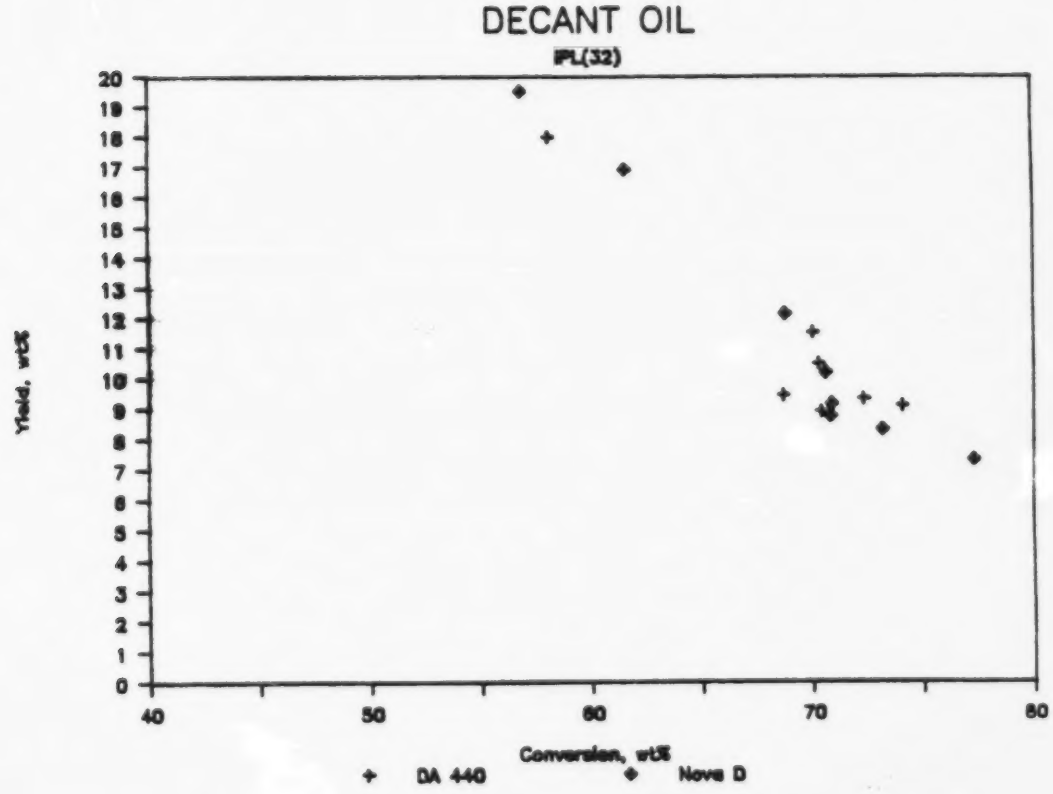

C5+ Gasoline Selectivity -- IPL & DA 440 --32WHSV
C5+ Gasoline Yield, wt%
55
50
45
40
35
50
60
70
80
Conversion, wt%
470 C
490 C
510 C

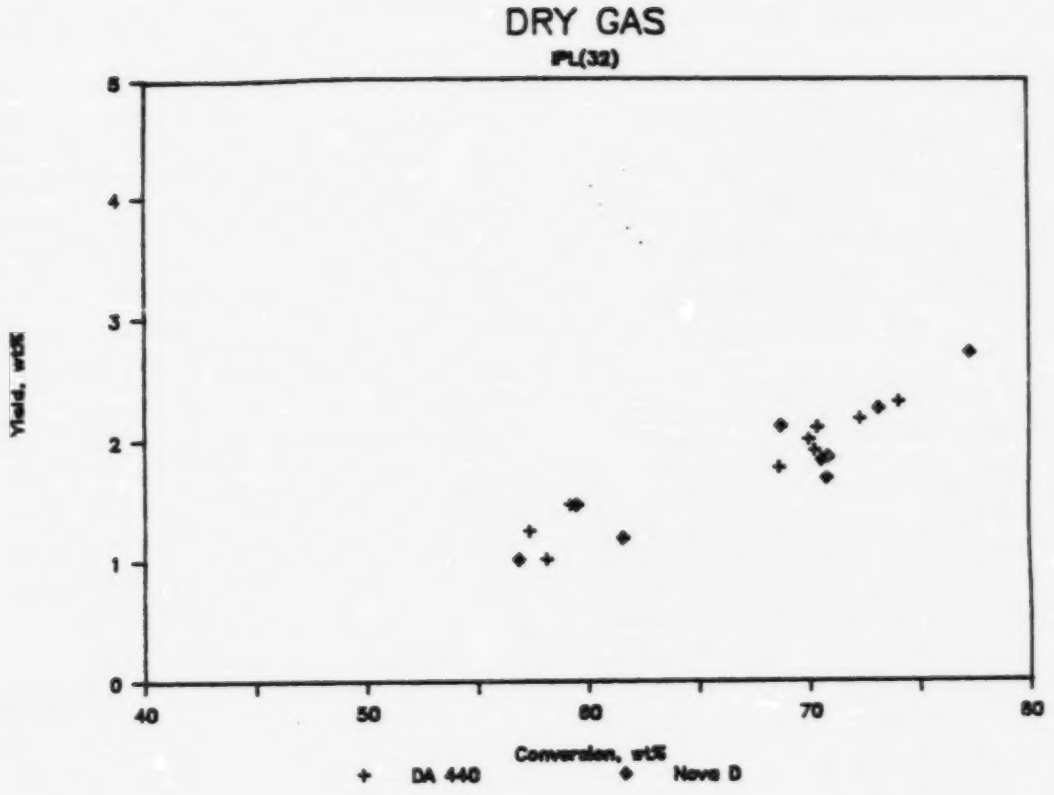

C5+ Gasoline Selectivity -- IPL & Nova D -- 32WHSV
C5+ Gasoline Yield, wt%
55
50
45
40
35
50
60
70
80
Conversion, wt%
470 C
490 C
510 C

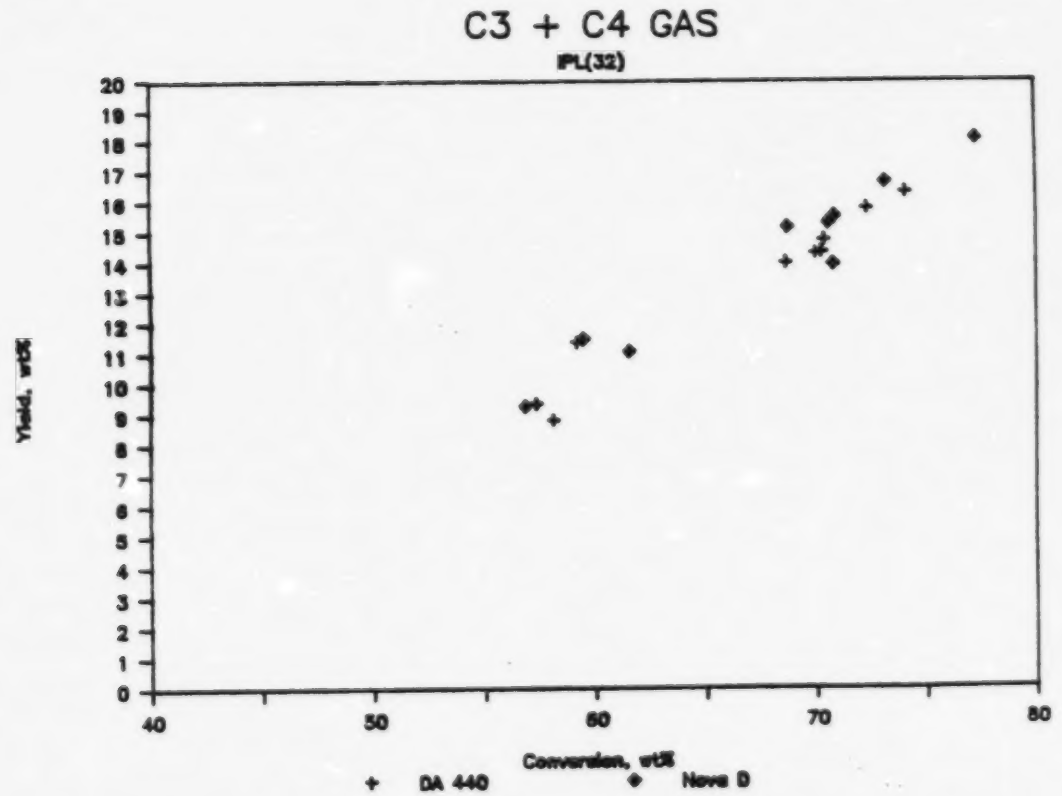

IPL(32) & DA 440
Conversion, wt%
80
75
70
65
60
55
50
45
40
0
2
4
6
8
Catalyst/Oil Ratio
+ 470
◇ 490
△ 510

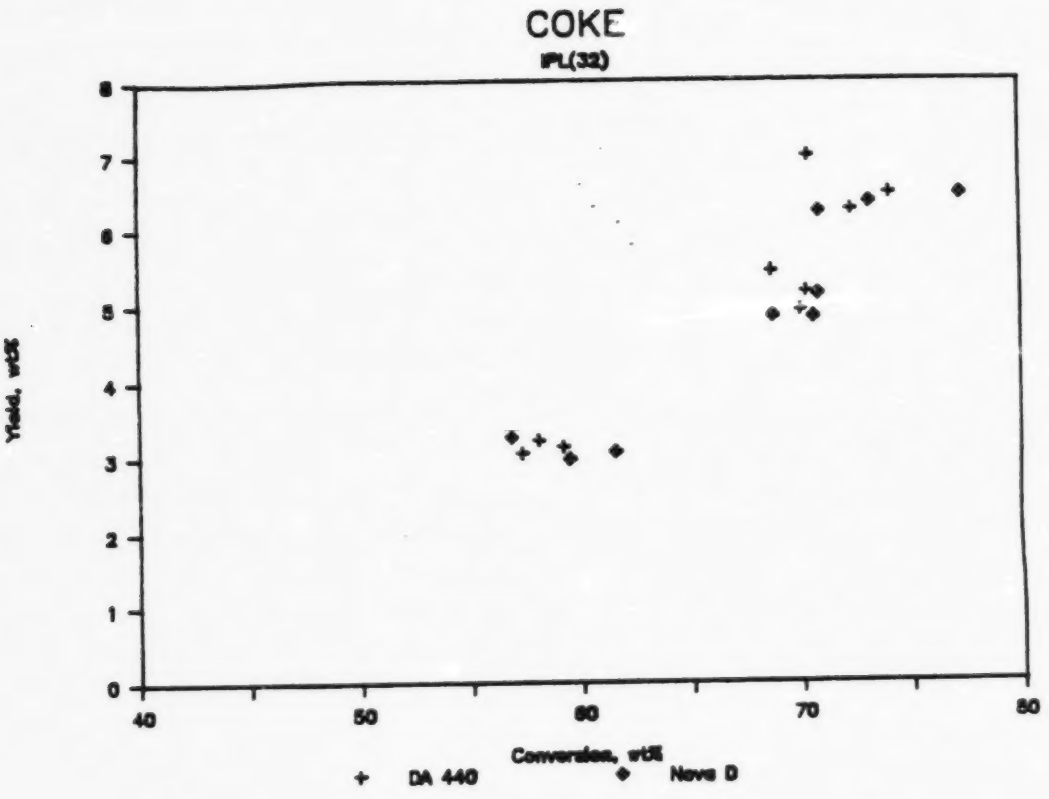

IPL(32) & Nova D
Conversion, wt%
80
75
70
65
60
55
50
45
40
0
2
4
6
8
Catalyst/Oil Ratio
+ 470
◇ 490
△ 510

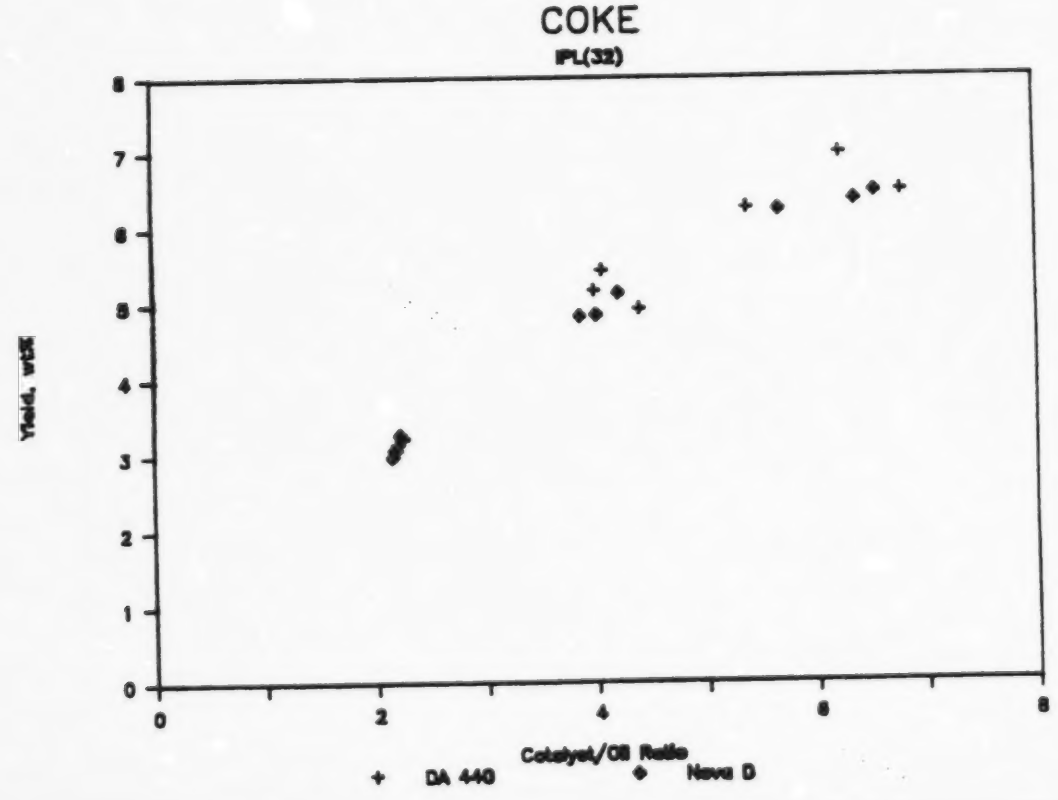

CYCLE OIL
IPL(32)
Yield, wt%
40
35
30
25
20
15
10
5
0
40
50
60
70
80
Conversion, wt%
DA 440
Nova D


DECANT OIL
IPL(32)
Yield, wt%
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
40
50
60
70
80
Conversion, wt%
DA 440
Nova D


DRY GAS
IPL(32)
Yield, wt%
0
1
2
3
4
5
40
50
60
70
80
Conversion, wt%
DA 440
Nova D


C3 + C4 GAS
IPL(32)
Yield, wt%
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
40
50
60
70
80
Conversion, wt%
DA 440
Nova D


COKE
IPL(32)
Yield, wt%
Conversion, wt%
DA 440
Nova D


COKE
IPL(32)
Yield, wt%
Catalyst/Oil Ratio
DA 440
Nova D

MICROACTIVITY TEST RESULTS USING
DA-440 EQUILIBRIUM CATALYST AND
IPL GAS OIL

RUN NO.	152	154	168	146	158	150	136	170	144
Reactor TempC	470	470	470	490	490	490	510	510	510
WHSV HR-1	18.60	19.60	20.20	18.80	19.10	19.50	17.50	19.40	20.20
C/O	1.92	3.66	5.30	1.90	3.76	5.49	2.04	3.67	5.37
Conversion	61.36	74.30	77.11	62.63	73.26	76.66	64.93	73.35	77.61
iC4/C4=	1.38	1.71	2.02	1.34	1.48	1.76	1.18	1.30	1.47
iC5/C5=	2.24	3.65	6.95	2.09	3.29	3.73	1.76	2.68	3.13
iC4C5/C4C5=	1.73	2.40	3.30	1.65	2.10	2.43	1.43	1.79	2.04

MICROACTIVITY TEST RESULTS USING
NOVA D EQUILIBRIUM CATALYST AND
IPL GAS OIL

RUN NO.	153	155	161	147	149	151	139	141	145
Reactor TempC	470	470	470	490	490	490	510	510	510
WHSV HR-1	18.60	18.60	20.10	17.60	18.50	18.00	18.10	19.20	18.30
C/O	1.92	3.83	5.40	2.03	3.83	5.97	1.96	3.74	5.87
Conversion	57.15	74.75	76.77	63.28	74.27	78.66	64.20	74.39	79.10
iC4/C4=	1.38	1.59	1.73	1.17	1.32	1.76	1.02	1.17	1.46
iC5/C5=	1.75	3.24	5.11	1.59	2.69	3.86	1.38	2.13	3.27
iC4C5/C4C5=	1.55	2.17	2.70	1.35	1.80	2.44	1.18	1.54	2.04

MICROACTIVITY TEST RESULTS USING
DA-440 EQUILIBRIUM CATALYST AND
IPL GAS OIL - 32 WHSV

RUN NO.	13	10	14	18	17	20	26	22	25
Reactor TempC	470	470	470	490	490	490	510	510	510
WHSV HR-1	28.50	31.60	29.50	29.40	32.00	34.20	33.80	29.00	27.10
C/O	2.25	4.06	6.23	2.18	3.99	5.38	2.20	4.40	6.78
Conversion	58.10	68.68	70.40	57.35	70.27	72.34	59.20	70.01	74.08
iC4/C4=	1.34	1.77	1.98	1.23	1.52	1.71	1.12	1.29	1.43
iC5/C5=	3.60	4.75	7.11	1.76	3.53	3.99	1.81	2.37	3.24
iC4C5/C4C5=	2.08	2.52	3.20	1.45	2.13	2.41	1.40	1.71	2.05

MICROACTIVITY TEST RESULTS USING
NOVA D EQUILIBRIUM CATALYST AND
IPL GAS OIL - 32 WHSV

RUN NO.	12	11	15	19	16	21	27	23	24
Reactor TempC	470	470	470	490	490	490	510	510	510
WHSV HR-1	28.90	32.20	32.50	29.50	3.10	29.80	29.40	31.50	28.90
C/O	2.22	4.21	5.67	2.17	3.86	6.36	2.15	4.01	6.54
Conversion	56.86	70.82	70.88	61.55	70.60	73.17	59.48	68.75	77.29
iC4/C4=	1.20	1.51	1.68	1.05	1.29	1.47	0.91	1.11	1.32
iC5/C5=	1.98	3.04	4.33	1.79	3.02	3.73	1.36	2.08	2.84
iC4C5/C4C5=	1.51	2.05	2.45	1.37	1.80	2.15	1.10	1.45	1.85

MICROACTIVITY TEST RESULTS USING
BA-440 EQUILIBRIUM CATALYST AND
LLOYD GAS OIL

MICROACTIVITY TEST RESULTS USING
NOVA B EQUILIBRIUM CATALYST AND
LLOYD GAS OIL

RUN NO.	84	86	88	78	80	82	72	74	76	83	85	89	77	79	81	71	73	75
Reactor TempC	470	470	470	490	490	490	510	510	510	470	470	470	490	490	490	510	510	510
WHSV HR-1	20.00	20.50	21.00	19.80	19.60	20.40	20.00	19.50	19.00	19.70	19.70	20.00	19.60	19.80	20.30	19.80	20.00	20.00
C/O	1.96	3.77	5.57	1.96	3.99	5.71	1.94	4.00	6.20	1.97	3.97	6.01	1.97	3.89	5.62	1.95	3.91	5.88
Conversion	50.96	59.48	63.71	54.40	64.00	66.55	54.82	64.70	69.13	51.13	60.40	63.67	51.94	59.97	64.99	52.72	60.97	66.86
iC4/C4=	1.34	1.57	1.74	1.27	1.53	1.67	1.18	1.35	1.64	1.27	1.46	1.66	1.12	1.37	1.50	0.98	1.24	1.40
iC5/C5=	1.63	2.88	3.02	1.58	2.56	3.13	1.58	2.34	3.10	1.45	2.49	3.11	1.34	2.23	2.76	1.28	1.77	2.76
iC4C5/C4C5=	1.47	2.05	2.22	1.41	1.92	2.19	1.35	1.72	2.17	1.35	1.85	2.18	1.22	1.70	1.95	1.11	1.46	1.86

MICROACTIVITY TEST RESULTS USING
DA-440 EQUILIBRIUM CATALYST AND
SUNCOR GAS OIL

RUN NO.	48	49	51	42	45	46	37	35	39	47	50	52	41	43	44	38	36	40
Reactor TempC	470	470	470	490	490	490	510	510	510	470	470	470	490	490	490	510	510	510
WHSV HR-1	19.50	19.60	17.90	19.50	20.60	18.90	19.90	19.80	20.00	17.60	19.70	19.20	19.20	19.40	19.80	19.40	19.40	20.40
C/O	2.02	4.00	6.49	2.05	3.80	6.26	1.95	4.04	5.81	2.24	3.94	5.85	2.06	4.13	5.94	2.03	4.12	5.87
Conversion	53.75	60.01	65.42	56.11	62.76	66.95	59.82	64.98	69.12	53.88	58.68	63.84	54.77	61.54	65.29	57.21	63.72	67.08
iC4/C4=	1.70	1.71	1.95	1.40	1.53	1.74	1.33	1.47	1.69	1.36	1.63	1.75	1.35	1.45	1.60	1.13	1.39	1.50
iC5/C5=	2.34	3.22	4.50	1.94	2.27	4.00	1.93	2.50	3.17	1.99	2.85	4.19	1.83	2.30	3.19	1.43	2.26	2.95
iC4C5/C4C5=	1.98	2.26	2.77	1.64	1.85	2.48	1.57	1.86	2.22	1.62	2.09	2.52	1.57	1.79	2.16	1.26	1.72	2.05

MICROACTIVITY TEST RESULTS USING
NOVA D EQUILIBRIUM CATALYST AND
SUNCOR GAS OIL

MICROACTIVITY TEST RESULTS USING
DA 440 EQUILIBRIUM CATALYST AND
COLEVILLE GAS OIL

RUN NO.	54	56	58	60	62	64	66	68	70	53	55	57	59	61	63	65	67	69
Reactor TempC	470	470	470	490	490	490	510	510	510	470	470	470	490	490	490	510	510	510
WHSV HR-1	19.30	17.60	19.80	19.10	20.30	20.00	19.30	19.60	18.80	19.10	19.40	19.20	19.30	19.70	19.90	19.30	19.30	20.10
C/O	2.01	4.40	5.67	2.03	3.85	5.90	2.00	3.95	6.07	2.05	3.98	5.87	2.02	3.93	5.74	2.00	4.00	5.79
Conversion	58.58	67.72	69.01	62.17	67.83	70.92	65.30	70.86	73.99	56.14	62.67	67.05	59.43	64.96	68.98	63.56	68.93	72.64
iC4/C4=	1.58	1.87	1.92	1.43	1.63	1.85	1.34	1.58	1.89	1.48	1.62	1.75	1.31	1.49	1.62	1.20	1.27	1.56
iC5/C5=	2.23	3.91	3.57	2.39	3.06	4.40	2.30	3.26	4.50	2.01	2.66	3.10	1.88	2.66	3.07	1.77	2.33	2.93
iC4C5/C4C5=	1.87	2.56	2.53	1.82	2.15	2.64	1.71	2.16	2.68	1.72	2.02	2.26	1.55	1.92	2.14	1.43	1.65	2.04

MICROACTIVITY TEST RESULTS USING
DA 440 EQUILIBRIUM CATALYST AND
SHALE OIL GAS OIL

RUN NO.	90	92	94	96	98	100	102	104	106
Reactor TempC	470	470	470	490	490	490	510	510	510
WHSV HR-1	19.10	19.90	19.60	18.70	19.00	19.80	19.10	17.70	19.20
C/O	2.05	3.93	5.92	2.07	4.03	5.86	2.05	4.31	5.85
Conversion	16.14	26.44	37.52	19.20	30.27	39.65	22.25	36.41	44.26
iC4/C4=	1.20	1.23	1.25	0.93	1.02	1.08	0.78	0.91	0.96
iC5/C5=	1.57	1.66	1.55	1.09	1.27	1.59	1.07	1.21	1.34
iC4C5/C4C5=	1.37	1.42	1.40	1.01	1.14	1.31	0.91	1.05	1.13

MICROACTIVITY TEST RESULTS USING
NOVA D EQUILIBRIUM CATALYST AND
SHALE OIL GAS OIL

RUN NO.	89	91	93	95	97	99	101	103	105
Reactor TempC	470	470	470	490	490	490	510	510	510
WHSV HR-1	18.90	18.90	19.40	18.60	18.60	19.40	18.90	19.00	19.00
C/O	2.05	4.10	5.96	2.08	4.12	5.97	2.05	4.03	5.92
Conversion	16.06	25.85	34.13	18.49	28.89	37.17	21.89	31.08	40.75
iC4/C4=	1.16	1.18	1.22	0.86	0.98	1.06	0.80	0.82	0.90
iC5/C5=	1.51	1.43	1.38	1.22	0.98	1.20	1.07	0.97	1.13
iC4C5/C4C5=	1.31	1.30	1.30	1.01	0.98	1.13	0.92	0.89	1.01

MICROACTIVITY TEST RESULTS USING
DA 440 EQUILIBRIUM CATALYST AND
CANMET FR3 GAS OIL

RUN NO.	180	178	192	174	172	190	188	186	184
Reactor TempC	490	490	490	510	510	510	530	530	530
WHSV HR-1	20.90	23.20	23.50	21.60	21.40	22.60	21.20	22.30	22.80
C/O	2.04	3.66	5.83	1.86	3.50	6.06	2.09	3.98	5.66
Conversion	20.33	33.87	47.13	21.82	34.57	52.91	27.00	42.26	51.20
iC4/C4=	0.99	1.02	1.10	1.10	0.92	1.02	0.78	0.84	0.94
iC5/C5=	1.51	1.56	1.73	1.14	1.35	1.71	1.19	1.26	1.55
iC4C5/C4C5=	1.21	1.23	1.35	1.12	1.10	1.29	0.94	1.01	1.18

MICROACTIVITY TEST RESULTS USING
NOVA D EQUILIBRIUM CATALYST AND
CANMET FR3 GAS OIL

RUN NO.	196	179	177	193	173	171	191	189	187	195
Reactor TempC	530	490	490	490	510	510	510	530	530	530
WHSV HR-1	23.2	21.30	21.80	23.20	21.10	21.30	23.20	21.00	22.50	23.00
C/O	5.91	2.00	3.66	5.90	1.77	3.37	5.71	2.12	3.97	5.94
Conversion	54.45	18.71	28.98	43.67	18.54	29.47	44.20	24.40	38.53	49.17
iC4/C4=	0.92	0.93	0.99	1.03	0.81	0.86	0.89	0.72	0.74	0.82
iC5/C5=	1.48	1.20	1.37	1.49	1.63	1.50	1.04	0.90	1.13	1.23
iC4C5/C4C5=	1.14	1.05	1.15	1.22	1.09	1.09	0.96	0.80	0.89	0.99